Dynamic Simulation Based on a Simplified Model of 1/3 Coking Coal Molecule and Its Formation Characteristics of Hydration Films

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ABSTRACT: To comprehensively elaborate the formation characteristics of hydration films on 1/3 coking coal molecule, this paper reports the construction of a realistic simplified model for calculations of electrostatic potentials on the coal molecular surface to foresee the major immersion locations. On this basis, interactions at the interface of coal molecules with different numbers of water molecules and their effects on each functional group of coal molecules were investigated. Using the scanning electron microscopy experiment, changes in the coal matrix before and after water leaching were compared and analyzed by fractal dimension calculations. Hydration characteristics of coal were described from a combined macroscopic and microscopic perspective. The results showed that both positive and negative electrostatic potential of coal molecules occurred near the O-containing functional groups. The hydroxyl group’s electrostatic potential (−OH) rose, resulting in higher electrostatic potential in coal–water molecules and providing many immersion sites. Deficiency in water molecules led to the complete immersion of water molecules. The interface of coal molecules could not be covered entirely, which led to the low number of active sites and Z values. The interface of coal–water molecules did not affect the average bond lengths of water molecules but decreased the bond angle by 3−4°. The influence of water molecules on the −OH groups of coal molecules was the most prominent when water molecules were incorporated into the coal molecules. Water damage for the coal matrix is more pronounced than in the raw coal itself. In view of above research, the formation characteristics of the hydration film from a microscopic point of view explained that the initial hydration of coal molecules was owing to H-bonds. From a macroscopic perspective, it was mainly due to structure changes for the coal matrix. This provides valuable references for field experiments in hydraulic fracturing and perforation.

1. INTRODUCTION

1/3 coking coal exhibits high volatile contents and strong coking properties.1−2 Some O-containing functional groups (including −OH, COOH, C==O, and C−O−C) may also be present in this coal.3 The amount of O-containing active groups is the critical factor influencing the different moisture contents of the coal molecules. Their chemical activity is relatively high, with hydroxyl groups being the most pronounced.4−5 Compared to lignite, this coal species is not more hydrophilic than lignite and does not easily cause the aqueous system’s hydration.6−8 Because lignite has large moisture (15−60%) and is mainly used for power generation, while 1/3 of coking coal is mainly used for coking and tailings treatment and has a high degree of development and metamorphism, with hydrophilicity of 4−20%, exhibiting less porosity and closing some pores, its hydrophilic capacity is relatively weaker than that of lignite.9 However, there are still hydrophilic groups on the coal matrix surface and even locally of 1/3 coking coal, resulting in uneven water distribution on the coal matrix surface, and the hydration membrane can be formed near these hydrophilic groups to hinder gas, diffusion, and penetration. In addition, moisture contents are very important to the formation of hydration films. Through high-pressure water injection in coal mine, hydration films will be formed on the surface of the 1/3 coking coal matrix in order to reduce gas adsorption capacity, replace gas, and improve the extraction rate. Therefore, studying the hydrophilic capacity of 1/3 coking coal has an essential supporting role, which can provide a certain theoretical basis for hydraulic and efficient gas extraction.10 Currently, coal–water adsorption systems have been studied more experimentally, but the properties of hydration films formed by water molecules after immersion into coal molecules cannot be obtained from the microscopic perspective,11,12 which is only elaborated from the perspective of the interaction between coal and water molecules via
molecular dynamic simulation methods, ignoring the structure of the functional groups contained in coal molecules. In contrast, Fourier transform infrared spectroscopy (FT-IR) provides insights on the functional groups. This method is straightforward and is used for qualitative and semiquantitative coal structure analyses. By the way of examples, Meng et al. tested the functional groups of coking coal samples using FT-IR experiments and analyzed the effect of kaolin addition on the pyrolytic behavior. It was found that 5% kaolin could improve the mobility of this coal, mainly due to the decrease in the CH<sub>2</sub>/CH<sub>3</sub> ratios in the remaining coking coals and the significant effect of the ratio of the C=O and C==C bonds. Wang et al. studied the structural characteristics for different coal ranks using atomic force microscopy (AFM) and microFT-IR. Decreased aliphatic functional group contents with the increased coal rank are reported. At the same time, the aromatic group contents increased, while the CH<sub>2</sub>/CH<sub>3</sub> ratio decreased. Liu et al. used microFT-IR to investigate the correlation between bituminous coal’s chemical and hydrophobic properties. Typical opposite trends of the half volume ratios and contact angles of the functional groups were presented for low and high coal samples.

Molecular dynamic simulations are often implemented to analyze the adsorption reactions and capacities, and their processes describe the state of molecular motion and the overall nature of this system. Until now, it has been widely used in the study of adsorption and interfacial properties. Chen et al. studied the formation mechanism of lignite hydration films by molecular dynamic simulation and determined that the H-bonds between the water and coal molecules are 1.8 Å on average. Kalinichev and Kirkpatrick showed that the hydrophilicity of minerals strongly affects the formation of hydrated membranes through the hydration membrane model of different silicate minerals. Zhang and Yan analyzed the oxygen diffusion characteristics of lignite including moisture contents in the process of coal oxidation. It was found that the oxygen diffusion was caused by the transition of oxygen molecules between adjacent cavities in the coal matrix. You et al. studied the wettability of cyanide (NP-4) on anthracite. It was shown that as the NP-4 concentration increased, the contact angle first increased and then decreased at the critical micelle concentration. Zhang et al. verified that the presence of water in coal reduced the coal—methane interactions and was the main factor leading to coal swelling based on Monte Carlo (MC) and molecule dynamics (MD) simulation.

For lignite, dynamic simulation analysis and the formation properties of hydration films are more mature, while less research has been carried out for 1/3 coking coal. Based on these facts, in this manuscript the simplified model of an actual 1/3 coking coal molecule was constructed and the electrostatic potential on this coal structure was calculated to predict the main immersion sites. On this basis, the interactions of water molecules at the coal molecular interface and their effects of individual functional groups in coal molecules were investigated for different numbers of water molecules (50–500). The scanning electron microscopy (SEM) scanning experiments were used to obtain the coal matrix pattern before and after coal leaching by comparing the calculated fractal dimensions. Then, the hydration characteristics of coal were elaborated from the combination of macroscopic and microscopic perspectives.

2. EXPERIMENT AND SIMULATION

2.1. Preparation. Coal was sampled from coal mine, and the type belonged to 1/3 coking coal. After completing the sampling work, the fresh sample was stored in multiple sealed bags and transported to the laboratory for the indoor test, then crushed and sieved through a 200-mesh standard sieve. The proximate and ultimate analysis are listed in Table 1.

2.2. FT-IR Test. In this experiment, this sample was fully ground according to the ratio of 1:200 and pressed into 0.5 mm flakes. Then, it was dried in the oven for 6 h, and the temperature was set at 110 °C. The KBr compression method was adopted. The sample was tested in the Perkin Elmer spectrum GX instrument with a resolution of 4 cm<sup>−1</sup>, scanning speed of 0.2 cm/s, cumulative scanning of 16 times, and the default spectrum range of 4000–400 cm<sup>−1</sup>.

2.3. MD Simulations. According to the split-peak fitting data, a simplified model was constructed using Materials Studio (MS) Software. Optimization was performed by the Dmol<sup>3</sup> module. Exchange–correlation potential was set by generalized gradient approximation Perdew–Burke–Ernzerhof function. Effective core potentials and double numerical orbital basis group + orbital polarization function (DNP) base groups (Basic 4.4) were chosen. A self-consistent field (SCF) convergence criterion was 10<sup>−6</sup>. Multilevel density expansion was set to octupole. Multiwfn<sup>11,28</sup> and visual molecular dynamics (VMD) software<sup>29</sup> were used to plot the electrostatic potential of coal molecule. Before drawing, the model previously optimized by MS software was imported into Gaussian software, and the geometric structure was optimized again because using MS software could not calculate the surface electrostatic potential and show any value of surface area. In Gaussian software geometry operation, the job type was used—optimization + frequency; the method was set—ground state, density functional theory, default spin, and B3LYP; and the basis set was chosen—6-31G(d). After optimization using Gaussian software, the structure would be changed. Then, a new structure was imported into Multiwfn Software to carry out to perform quantitative analysis, and the surface electrostatic potential was set to 0.001 for electron density and 0.25 Bohr for lattice spacing. Surface area distribution in the range of −189–268.8 kJ/mol was calculated. The extreme point, vertex, and geometry files of the surface were imported into VMD to plot the electrostatic potential distribution.

Then, the optimized coal molecules were placed into the crystal cell in MS software. Use the AC module to add 15 coal molecules (corresponding to 1605 atoms) and construct periodic boundary, after continuous optimization and adjustment, the final boundary cell size of the model was 25.5 Å × 25.5 Å × 25.5 Å, and the target density was 1.2 g/cm<sup>3</sup>.

Using the established model, a vacuum layer of 30 Å was added, and water molecules were placed, with the numbers of
Figure 1. FT-IR spectra. (a) Total spectrum, (b) 3700–3000 cm$^{-1}$, (c) 3000–2800 cm$^{-1}$, (d) 1800–1000 cm$^{-1}$, and (e) 900–700 cm$^{-1}$.
water molecules ranging from 50 to 500. Energy minimization was carried out with a cut-off radius of 15.5 Å before performing MD calculations. The COMPASS force field was chosen for the NVT dynamic simulations performed at 298 K, 1 ns simulation time, and 1 fs step size. Total simulation time was set 1000 ps. The electrostatic interaction energy and van der Waals interaction energy were calculated using Ewald and Atom Based, respectively.

2.4. Calculation Method of Radial Distribution Function. Radial distribution function (RDF) was often used to characterize the particle microstructures and reflect the particle aggregation. It could also be interpreted as the bulk densities of this system. The calculation expression is shown in eq 1.

\[ g_{ab}(r) = \frac{dN}{4\pi\rho_b r^2 \, dr} \]  

where \( dN \)—the number of \( b \) particles in the distance to a particle in the range from \( r \) to \( r + dr \) and \( \rho_b \)—density of \( b \) particles.

3. RESULTS

3.1. Fourier Transform Infrared. The FT-IR spectrogram (Figure 1a) is divided into four regions belonging to the \(-\text{OH}\) groups (3700–3000 cm\(^{-1}\)), aliphatic hydrocarbons (3000–2800 cm\(^{-1}\)), O-containing groups (1800–1000 cm\(^{-1}\)), and aromatics (900–700 cm\(^{-1}\)). OMNIC software was used to calibrate the baseline of each part and peak fitting. The fitting data are normalized to calculate these functional groups (Figure 1b–d).

According to the element analysis and infrared spectrum assignment, O-containing groups were primarily \(-\text{OH}, \text{C}–\text{O}–\text{C}, \text{COOH}, \text{and C}–\text{O}–\text{O}\). Peaks at 900–700 cm\(^{-1}\) indicated the appearance of 2-substituted aromatic hydrocarbons (4H). The peaks in the 3482–3414 cm\(^{-1}\) range confirm H-bond presence. The fatty chain exists in the form of methylene.

Thus, elemental analysis and FT-IR data confirmed that the molecular formula could be expressed as \( \text{C}_{49}\text{H}_{46}\text{O}_{10}\text{N}_{2} \) (Figure 2). Heteroatoms were not considered because of the low sulfur contents. Moreover, the \(-\text{OH}/\text{C}–\text{O}–\text{C}/\text{COOH}/\text{C}–\text{O}–\text{O} \) group ratio was 5:2:1:1. The larger cyclic units are formed by ether and methylene groups.

3.2. Surface Electrostatic Potential. Of course, the structure of coal molecules optimized by Gaussian software will inevitably change (Figure 3). O-containing groups are present in this new coal molecule. They form H-bonds with water molecules, creating a favorable environment for electrostatic adsorption, which determines interactions between the coal and water molecules. Thus, calculating the distribution of electrostatic potential could foresee overall system structure of this coal molecule.

Oxygen atoms themselves have a pair of lone electrons and are highly electronegative. Therefore, potential of oxygen atoms is very low (−156.324 kJ/mol). When the hydrogen atom is attached to the oxygen atom, a significant negative potential (−156.324 kJ/mol) is generated. The pole of the electrostatic potential is near the O-containing functional groups, which interact more easily with water molecules than other groups. Meanwhile, a certain amount of negative potential (about −73.584 kJ/mol) appears around the C–O–CH\(_3\), if C–O–CH\(_3\) combines with water molecules to form weak hydrogen bonds.

When water molecules appear, they are placed near the absolute value of maximum negative potential (−185.556 kJ/mol). Then, the geometry optimization is recalculated to achieve the most stable system to determine the specific surface areas of different surface electrostatic potentials in the water molecules’ free state (Figure 4). The positive electrostatic potential area (about 120Å) of water molecules immersed in the coal molecular structures increases substantially, mainly because the oxygen atom in water molecule combines with −OH groups in this coal molecule to form H-bonds and brings the hydrogen atoms to the surface. Water
molecule is polar molecule, and the rise in the electrostatic potential of $-\text{OH}$ groups and surface electrostatic area due to the constant bond angle directly results in the increase in electrostatic potential in the mixture system of coal–water molecules.

3.3. Interaction Relationships between Coal and Water Molecules. 3.3.1. Structural Balance and Average Energy Change for Water Molecules. Based on Figure 2 and Section 2.3, the periodic boundary model of adding 15 coal molecules is placed in the cell (Figure 5).

![Figure 5. Boundary condition model (25.5 Å × 25.5 Å × 25.5 Å).](image)

Using the original model as a setup, different amounts of water molecules and vacuum layers are added with NVT equilibrium to achieve stability. After dynamic simulations, when the number of water molecules is 50, it is basically "immersed" in coal molecules, and no water molecule layers are formed (Figure 6a). When over 100 and 150 water molecules are present, the coal molecules are completely covered with the transparent water molecular layer (Figure 6b,c). The thicknesses of the water molecular layer increase as the number of water molecules add (Figure 6d–j).

After establishing the layered structure of different water molecules and the corresponding water molecular layers around the structure of coal molecules, the average interaction energies of water molecules could be obtained from eq 2.

$$E_{\text{average}} = \frac{E - E_{\text{coal}} - E_{\text{H}_2\text{O}}}{n}$$

Note: $E_{\text{average}}$—average interaction energies of water molecules; $E$—energies of coal–water molecules after steady state; $E_{\text{coal}}$—energies of coal molecules; $E_{\text{H}_2\text{O}}$—energies of water molecules; and $n$—number of water molecules.

Table 2 and eq 2 demonstrate that the average interaction energies of water molecules between coal and molecules can be described as non-bond energies, van der Waals interaction energies, electrostatic energies, and long-range effects. After the dynamic calculation reaches stability, it is found that the average interaction energies of water between coal molecules and water molecules are mainly non-bond energies, and these values are less than 0. When the numbers of water molecules are 100 and 150, the average energies of water molecules are $-11.96$ and $-6.34$ kJ/mol, respectively. However, there are large differences between 50 water molecules and 150 water molecules, mainly because 50 water molecules are completely immersed in coal molecules, and some of 100 and 150 water molecules are active on the surface of coal molecules. The average interaction energies of 150 and 200 water molecules are relatively close, indicating that the overall average

![Figure 6. Dynamic equilibrium for different water molecules under surface action of coal molecules. (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, (f) 300, (g) 350, (h) 400, (i) 450, and (j) 500 water molecules.](image)
interaction energies of the two are basically the same. All in all, the average electrostatic energies of water molecules are larger than those of van der Waals interaction energies, and the long-range effects account for only small parts of the energies. It is proved that water molecules are immersed in the main functional groups of coal molecules through electrostatic actions, which provide guarantee for the subsequent calculation of water molecular diffusion coefficient, concentration, density, and RDF.

### 3.3.2. Concentration and Density

As shown in Figure 7, the concentration of water molecules mainly reflects their distribution over the whole system and their density related to the total density in a specific range. According to dynamic simulation results and interfacial distance distribution of coal-water molecules, water can be classified as dispersed water, interface water, and free water. Among them, the free water refers to the free movement of water molecules, dispersed water is the layer of water away from the coal and water molecules, and interfacial water is the layer of water molecules bound to the coal molecules by hydrogen bonding and electrostatic energy near the water molecules in the solid-liquid interface.

When only 50 water molecules are presented on the coal surface, the concentration peak is near the position of about $Z = 39.34$ Å, which is close to the lowest value of the model surface. When there are fewer water molecules, the concentration and density of water molecules immersed inside the coal molecules will have corresponding peaks, based on the principle of minimum energy. Thus, when not enough water molecules are present to cover the surface of coal molecules, the concentration value corresponds to the smallest Z-value and is most easily absorbed. At higher water molecules, the immersion sites of coal molecules become entirely covered by water molecules through $-$OH or H-bonding. The peak concentration formed decreases, and the Z-value corresponding to the peak position increases (Figure 7a). At the number of water molecules above 500, no prominent peaks are observed, and the density of the adsorbed water molecular layer is equal to that of bulk water (Figure 7b). At this time, the effect of water molecules on the upper layer of coal molecules could be ignored. The interfacial water distribution is the same as the bulk water with the density $\rho = 1$ g/cm$^3$.

### 3.3.3. Diffusion Coefficient

A diffusion coefficient ($D_i$) is obtained in eq 3 using mean square displacement (MSD) and Einstein equation.\(^{37}\)

$$D_i = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2$$  \(3\)

Note: $N$—number of the particles; $t$—simulation time; and $r_i(t)$ and $r_i(0)$—position vectors at $t$.

The MSD–T curve is made, a straight-line $y = ax + b$ is selected, and the slope $a$ is recorded, then the diffusion coefficient is $D_i = a/6$. The corresponding diffusion coefficients at different numbers of water molecules are shown in Figure 8a. Also, the relationships between the diffusion coefficients and the surface areas for the different numbers of water molecules are presented (Figure 8b).

As listed in Tables 3 and 4, considering the complex structure of coal molecules, when the water and coal molecules interface with each other, the number of water molecules is low (50 water molecules), then the coal molecules are completely invaded, corresponding to a higher relative concentration and lower density, which enhances the mobility of water molecules within the coal molecules, then the diffusion coefficient and specific surface area will also be larger. As the number of water molecules continues to grow, when reaching 100, it effectively changes the flow area of water, producing a certain thickness of the interface so that a hydration film is formed. At this time,

![Figure 7](https://doi.org/10.1021/acsomega.1c03345)  
Figure 7. Relative concentration and density for water molecules adsorbed on the coal molecules. (a) Relative concentration, (b) density.
the peak relative concentration is still lower, corresponding to increases in the $Z$-value distance and density. At higher water molecules (equal to $100-500$), their thicknesses also rise significantly (Figure 6). Simultaneously, the diffusion coefficients and specific surface areas rise significantly (Figure 8b), but the relative decrease in the free volume of coal molecules occupied by water molecules is primarily because of “the saturation of coal molecules by water molecules.” Overall, the immersion sites from the interface between water and coal molecules determine the changes in the internal structure of coal molecules when dynamic simulations are performed. The changes in their concentrations and densities are strongly affected by the number of water molecules, which directly affect the immersions and diffusions.

3.3.4. Bond Lengths and Angles of Water Molecules. H-bond lengths and angles strongly depend on the intermolecular interactions. The bond lengths (O–H) and angles (H–O–H) of stand-alone water molecules (before any calculations) were set as 0.98 Å and 104.51°, respectively. The calculation method still uses Dmol3 for geometric optimization in MS. After their calculations, the two values are 0.971 Å and 103.627° (Figure 9).

Bond lengths and angles of water molecules under interactions of coal–water molecules are close to those for a single water molecule before and after optimization (Figure 10a), and all peak values under different water molecules are near to 0.971–0.98 Å. However, the peaks of bond angle distribution curve are about 3.5–4.5° smaller than $\theta$ (103.627°) except for the 50 water molecules. When there are 50 water molecules in coal molecules, the interface of coal molecules cannot be covered entirely. Thus, most water molecules are present in the adsorbed state. According to Figure 10b, when 50 water molecules are immersed, the bond angle is closer to 103.627° than the other nine groups of water molecules. Relative to the bond length, the H-bond does not affect the O–H binding energy. No matter how many water molecules are added, the O–H bond length remains unchanged (0.971–0.98 Å). Thus, the interface structure of coal–water molecules does not affect the H–O bond length but indeed affects the H–O–H bond angle. Moreover, with the addition of the number and densities of water molecules, the bond angles of water molecules will also approach those of single water molecule.

3.4. Radial Distribution Function. The interfacial interactions of coal–water molecules and immersion influences of water molecules on various functional groups for coal molecules are analyzed using RDF.
First, the RDF between different molecules should be considered for the interfacial interactions of coal–water molecules. The atoms in water and coal molecules are labeled with the indices “w” (e.g., Ow and Hw) and “1/3C” (e.g., O_{1/3C} and H_{1/3C}).

The Ow–Ow in the water molecules describes their relative positions and order degrees. The peaks at 2.91 Å correspond to the first coordination ring between the corresponding water molecules (Figure 11a), which is equivalent to the distance between two oxygens in pure water, indicating that they...
probably do not influence the properties of water molecules, which are the same as bulk water at the interface of coal molecules. At \( r > 3.5 \text{ Å} \), the distribution of water molecules reaches equilibrium. At higher water molecules, effects of coal molecules on the water molecular layer become proportionally smaller. Thus, the number of water molecules does not depend on the \( \text{O}_w-\text{O}_w \) distance. Yet, the corresponding peaks \([g(r)]\) decrease.

As shown in Figure 11b, the first peak for \( \text{O}_w-\text{H}_w \) indicates that the average length of H-bonds between water molecules at the interface of coal—water molecules is equal to 1.95 Å. The second peak (at 3.27 Å) corresponds to the distance between the oxygen and the hydrogen in the water molecules. The first peak is stronger than the second peak. Thus, electrostatic energy of water molecules is stronger than the corresponding van der Waals interaction energy. The RDFs for the \( \text{O}_{1/3C}-\text{H}_w \) and \( \text{H}_{1/3C}-\text{O}_w \) demonstrates that the average H-bond length between water molecules is equal to 1.95 Å and the O-containing functional groups of coal molecules is 1.97 Å (Figure 11c,d). The second peak height (equal to 3.21 Å) is mainly a functional group marked with di-atom, which have a stronger charge effect than carbon atoms, so that the presence of nitrogen atoms also has a significant immersion effect on water molecules.

In addition, O61, O53, C51, O35, C34, and N60 have the highest values in hydroxyl, ether, carboxyl, carbonyl, methyl, and nitrogen functional groups, respectively, and the order of highest RDF peaks is \([-\text{OH}] (2.52 \text{ Å}) > [\text{N-S}] (1.65 \text{ Å}) > [-\text{CH}_3] (1.47 \text{ Å}) > [\text{C-O-C}] (1.29 \text{ Å}) > [-\text{COOH}] (1.08 \text{ Å}) > [\text{C}=\text{O}] (0.47 \text{ Å}) \). According to the average RDF curve, the order of average distance is \([-\text{OH}] (1.49 \text{ Å}) > [\text{N-S}] (1.29 \text{ Å}) > [\text{C-O-C}] (1.19 \text{ Å}) > [-\text{COOH}] (1.08 \text{ Å}) > [-\text{CH}_3] (0.88 \text{ Å}) > [\text{C}=\text{O}] (0.47 \text{ Å}) \). Water molecules are enriched around \([-\text{OH}] \) but disperse around \([-\text{CH}_3] \) and \([\text{C}=\text{O}] \). The peak values can reflect the best immersion abilities, and the peak value of \([\text{C}=\text{O}] \) is lower than that of \([-\text{COOH}] \) and \([\text{C}=\text{O}-\text{C}] \). It is proved that water molecules have the highest immersion abilities for \(-\text{OH} \) groups. The results are consistent with those in Section 3.2.

4. DISCUSSION

4.1. Coal Matrix Change Patterns. From the above microscopic simulation, the interactions between water and coal molecules and their effects on the individual functional groups are investigated, and their hydrated film formation properties cannot be explained purely from a microscopic perspective and are therefore described from a macroscopic (coal matrix) perspective. Most of relevant literature studies used mercury-pressure experiments to calculate the fractal dimensions and discussed the extent of water damage to coal, which can only react to the structural damage and cannot verify the extent of change in the coal structure before and after water immersion.\textsuperscript{38,39} In this paper, based on SEM scanning experiments, relevant cracks are extracted, and the fractal dimensions are calculated to explore the changing pattern before and after water intrusion, which provide further exploration opportunity to understand the characteristics of hydrated films.

According to GB/T 20307-2006 standard in China, a scanning electron microscope is used to observe the visual information about the microstructure of this sample at different magnifications, which is convenient for understanding the damage characteristics of the coal sample.\textsuperscript{40,41}

The raw coal samples and coal samples immersed in water after drying, 2−3 mm coal particles are directly screened out, and the microstructure and morphology characteristics of raw coal and soaked coal are observed at 800 and 1600 times to understand the change in the internal structure of the two coal samples. Through image processing, the micro-cracks in SEM images are obtained. Parts of the crack information are retained, and all irrelevant information is removed. The fractal dimension of cracks is calculated by fractal theory, and then, the failure characteristics of the two coal bodies are analyzed (Figure 14).

For calculation of the fractal dimension of cracks, it mainly represents an essential parameter of the coal pore interpenetration and the network complexity. The specific method...
Figure 13. Average RDF curves of functional groups at the interface of coal–water molecules (100H2O). (a) H2O-hydroxyl, (b) H2O-ether, (c) H2O-carboxyl, (d) H2O-carbonyl, (e) H2O-methyl, and (f) H2O-pyrole.
is to divide the image $P$ into several grids with side length, $\delta_n$, and calculate the number of grids $M(\delta_n)(P)$ covered by the binary image area. If image $P$ has fractal characteristics, it can be calculated according to eq 4. The fractal characteristics of the two coal samples are calculated.

$$D = \lim_{n \to \infty} \frac{\ln M(\delta_n)(P)}{\ln \delta_n}$$  \hspace{1cm} (4)

Note, $M(\delta_n)(P)$—the number of grids covering the binary image area.

Based on the above fractal calculation method, a box-dimension fractal calculation program is compiled. To eliminate the image grid “distortion,” the width and height of the image are set as equal, and the $\delta_n$ sequence is generated. 1024 × 1024-pixel area is selected to cover the processed SEM image. Then, the side lengths were divided by 2, and square boxes (regions) of 512, 256, 128, ..., 4, 2, 1, respectively, to cover the processed SEM image were used, and the square box sizes ($\delta_n$) covered by different side lengths were counted. The number of boxes in the cracked image ($M$) is drawn in the logarithmic coordinate system, and the $\ln M$–$\ln(1/\delta_n)$-relationship diagram is drawn. The slope $D$ of the straight-line fits according to the linear relationship represents the fractal crack image dimension.

The raw coal fractal dimensions are 1.33–1.38 and 1.37–1.45 under 800 and 1600 magnification, respectively (Figure 15). The crack fractal value of the same sample at 1600 times magnification is about 0.4–0.7 greater than that of 800 times. In addition to the more detailed observation of cracks at high magnification, the effect of water on coal cracks and pores is more evident than that of raw coal itself. It shows that the larger the value of crack fractal, the more pronounced the internal coal structure change. The main reason is that when water is immersed into the pore structure of coal, its seepage and capillary force change. The degree of water-free diffusion increases continuously. In a short time, the influence of seepage on the pore fracture space is related to injected water quantity and soaking time. Compared with raw coal, its pore size also changes significantly. Therefore, the formation of the hydration membrane is equivalent to the physicochemical interaction between coal and water. The increase in fractal
dimensions is exactly the erosion of coal and coal pore surface by water, which leads to the dispersion of minerals and changes in the surface morphology. On the one hand, the flow of gas in the pores is impeded, slowing down the rate of gas release; on the other hand, competitive adsorption occurs in the pores and occupies the position of oxygen-containing functional groups.

4.2. Formation Characteristics of Hydrated Films.
Considering the macroscopic perspective, the coal matrix itself has a dual structure of pores and fractures, which determines the difficulty of water infiltration. When water infiltrates into the coal matrix (coal molecules), the degree of pore and fracture development is evident (Figure 14), and water diffuses within the coal matrix (Figure 16). After water immersion, the coal matrix is very effective in terms of hydrophilicity, connectivity, and wetting, forming complex “network” channels and increasing fractal dimensions.

From microscopic analysis, during the dynamic simulation at the interface between coal and water molecules, dynamic properties of water molecules are influenced by the interface of coal—water molecules and the H-bond among water molecules (Figure 17a); when the water molecular layer is adsorbed on coal molecules, the original water molecule layer inside the H-bonding breaks the structural equilibrium, at this time the upper layer of water molecules in the coal—water molecules is not only concentrated in functional groups of coal molecules (mainly the hydroxyl group is dominant) or atoms but also with the interaction energy (electrostatic and van der Waals interactions) related to the water molecules between hydrogen bonding, which is less effective. When water molecules reach 100, they are entirely immersed in the coal. As the number of water molecules go on rising further, average number of H-bonds gradually approaches that of H-bonds in pure bulk water. Water molecules occupy many immersion sites in the coal molecules, making diffusion coefficients and specific surface areas increase with the number of water molecules, and the thicknesses also increase continuously when the hydration film gradually forms. As for the interaction among water molecules, H-bond lengths are different as opposed to the O–
H chemical bond. The corresponding peaks are not concentrated at a particular value (Figure 17b). When the number of water molecules is equal to 50, the larger peaks correspond to the H-bond length at this point, and the fewer H-bonds form. The peak weakens with the number of water molecules reaching from 100 to 500, the H-bond length between water molecules becomes almost 2 Å (Figure 11b,c). The more the number of water molecules, the more pronounced H-bonding effect becomes. However, the formation of the hydrated film is not altered by its overall water molecular structure.

In view of the above research and understanding, hydration film formation characteristics from a microscopic point of view show that the initial stage of hydration of coal molecules occurs through the O-containing functional groups. When the number of the surrounding water molecules increases, the effect of their H-bond becomes more apparent, which, in turn, results in the thickness increase of the water molecular layer and the formation of the hydration film, and the degree of structural changes at the coal—water interface is not only related to the O-containing groups (mainly −OH), H-bonds, electrostatic and van der Waals interactions but also directly affects the diffusive immersion of water molecules. However, the macroscopic perspective is mainly because water immersion changes the coal’s surface structure and continuously transforms the internal pores and fissures, leading to physicochemical structural changes, which are irreversible.

Therefore, if this phenomenon is taken into account in field engineering applications involving coal—water interface, the fracture of the coal is continuously enlarged or extended through the water flow, accompanied by new pores, increasing their permeability. Under water injection pressure conditions such as hydraulic punching and fracturing, the injection pressure and immersion time can alter the coal matrix itself. When a certain amount of gas is present in the coal, the presence of water can fully displace the gas, increasing the permeability of coal and reducing the difficulty of mining.

5. CONCLUSIONS

(1) By calculating electrostatic potential, both positive and negative electrostatic potential of 1/3 coking coal molecule occurred near the O-containing surface groups. Following the immersion of water molecules, the hydroxyl group’s electrostatic potential (−OH) rose, resulting in a higher electrostatic potential in the coal—water molecules and providing many immersion sites. The immersion of water molecules at the interface process of coal molecules was not only reflected in the O-containing surface groups of coal molecules but also in how many water molecules were presented and in their electrostatic energy distribution. Their concentrations and densities also directly affected the diffusions and immersions of water molecules in coal molecules.

(2) At lower water molecules, they were completely immersed in coal molecules and couldn’t completely cover the interface of coal molecules. The active sites and Z-values were low. At higher water molecules (100–500), the peak concentration decreased and the Z-value corresponding to the peak position increased. When water molecules were 500, the density of interfacial water was essentially the same as that of bulk water (1 g/cm³).

(3) Interface between coal and water molecules was influenced via ordered structure and independent of water molecules before and after optimization. The average O−H bond length was merely identical to individual water molecule. The corresponding bond angle was 3–4° below the angle value for single water molecule. As water molecules increased, the average hydrogen bond length remained essentially constant (1.97 Å). The effects of water molecules at the interface of coal—water molecules on the various functional groups of coal molecules were analyzed. The order of average RDF peak is −OH > N−S > C=O−C > COOH > −CH₃ > C==O. It was demonstrated that influences of water molecules on the hydroxyl groups were most obvious.

(4) The effects of water on coal cracks and pores were more pronounced than that on raw coal itself, as calculated by the fractal dimension. In view of the above research, formation characteristics of hydration films from a microscopic point of view showed that the initial stage of hydration of coal molecules occurs through the O-containing functional groups, and once water molecules gradually increased, their hydrogen bonding became more and more evident. From macroscopic perspective, it was mainly due to physicochemical properties of water that changed the surface structure of the coal matrix.

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Notes
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