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Experimental Study on the Influence of Wettability Alteration on Gas–Water Two-Phase Flow and Coalbed Methane Production

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Abstract: The surface wettability is important in the change in the relative permeability of gas and water. Due to the heterogeneous property of coal, it has a mixed wetting state, which makes it difficult to predict the change in permeability. To investigate the influence of different wettabilities on two-phase flow, a total of three different rank coal samples were collected and were treated with different chemicals. The alteration of the coal's wettability, characteristics of gas–water flow, and relative permeability of the coal after the chemical treatments were analyzed. The research conclusions suggest that (1) the coal samples treated with SiO₂ and H₂O₂ increased the hydrophilicity of the coal surface, while the coal samples treated with DTAB increased the hydrophobicity of the coal surface. Compared to SiO₂, both H₂O₂ and DTAB can form a uniform wetting surface. (2) The wettability alteration mechanism among the three different chemical reagents is different. (3) All the chemicals can change the gas–water interface. The water migrates more easily through the cleats after H₂O₂ treatment, while it is more difficult for the water to migrate through cleats after the DTAB treatment. (4) There are two types of flow states of gas and water on different wetting surfaces. A slug flow is formed on a hydrophilic surface, while an annular flow is formed on a hydrophobic surface. (5) The crossover point and the residual water saturation of the relative permeability curves were influenced by the surface wettability.

Keywords: coal wettability; gas–water flow; chemical treatment; gas production

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1. Introduction

The exploration, development, and utilization of coalbed methane (CBM) can alleviate the current energy shortage problem [1–3]. Not only can it solve the environmental pollution problems caused by a large amount of coal gas discharge into the atmosphere during the coal mining process [4,5], but it can also reduce accidents caused by gas outburst in coal mines underground [6,7]. Although significant breakthroughs have been made in the development of CBM worldwide, the current exploration and development of CBM still draws on conventional oil and gas development theories [8–10]. Many studies have shown that coal is water wet or hydrophilic according to the results of relative permeability measurements [11,12]. However, the problem with this result is that coal is different to rock which is homogeneous. Due to the heterogeneous property of coal, it has a mixed wetting state which is dependent on rank, maceral composition, mineralization, and surface topography [13–16].

The surface wettability is important in the change in the relative permeability of gas and water [17–19]. Due to the strong heterogeneity of coal, a layer of water film will adhere to the rough and narrow cleat channel surface in a hydrophilic coal fracture area, causing a water resistance effect [20,21]. This effect will hinder gas from passing through these areas until there is sufficient displacement pressure to drive water out of this

area [22–24]. By changing the wettability of the coal surface, a relatively uniform wetting surface can be obtained, which can effectively alleviate capillary effects and improve fluid permeability [25,26]. A study by Naik et al. showed that in the early stage of coalbed methane development, namely, the drainage stage, specific chemical reagents are used during drilling or fracturing to form a hydrophilic surface in the coal reservoir seepage channel, thereby reducing the amount of water trapped in the pore fractures during the drainage stage [27]. In the gas production stage, by changing the wettability of coal to transform it into a hydrophobic surface, the water blocking effect is reduced and the gas permeability in the seepage channel is improved [28,29]. At different production stages, by changing the wettability of the coal surface, the fluid permeability in the seepage channels of each stage is enhanced, ultimately improving the methane recovery rate of coalbed methane wells [30,31].

Previous researchers have conducted a lot of work in using chemical reagents to change the surface wettability of coal. Liu et al. demonstrated that electron-rich aromatic rings can be oxidized to form hydroxyl functional groups after being treated with hydrogen peroxide. The increase in hydroxyl functional groups makes the surface of coal more hydrophilic [32]. Liu's study showed that stronger oxidants can induce the production of carboxyl or aldehyde groups, which further increases the polar functional groups on the coal surface [33]. For the drainage and depressurization stage of coalbed methane, if the coal near the wellbore is hydrophilic, its water production rate and water yield will be improved. In terms of coal flotation, oxidants are also used to change the surface characteristics of coal and serve as a means of removing impurities [34,35]. In addition, Sadler used heated sodium hydroxide to dissolve the coal surface, thereby increasing the fracture width and absolute permeability [36]. However, in the study of using chemical reagents to improve the recovery rate of coalbed methane, the systematic research on the testing of different chemical reagents on coal samples with different degrees of metamorphism and different components is still at an early stage. So far, few scholars have specifically studied the influence of the change in surface wettability of chemically treated coal samples on the gas–water interface contact angle and residual water in the seepage channel of coal reservoirs, as well as the influence of the change in coal wettability on the relative permeability of coalbed methane.

In this paper, we investigated the effect of coal samples treated with different chemical reagents (SiO_2 , H_2O_2 , and DTAB (dodecyl trimethyl ammonium bromide)) on the wettability of coal. The influence of different wettability surfaces on the migration and distribution characteristics of gas–water two-phase flow in the microfracture system was analyzed, and the change law of gas–water relative permeability under different gas–water flow states was revealed. The above results can provide theoretical guidance for improving the production capacity of coalbed methane.

2. Materials and Methods

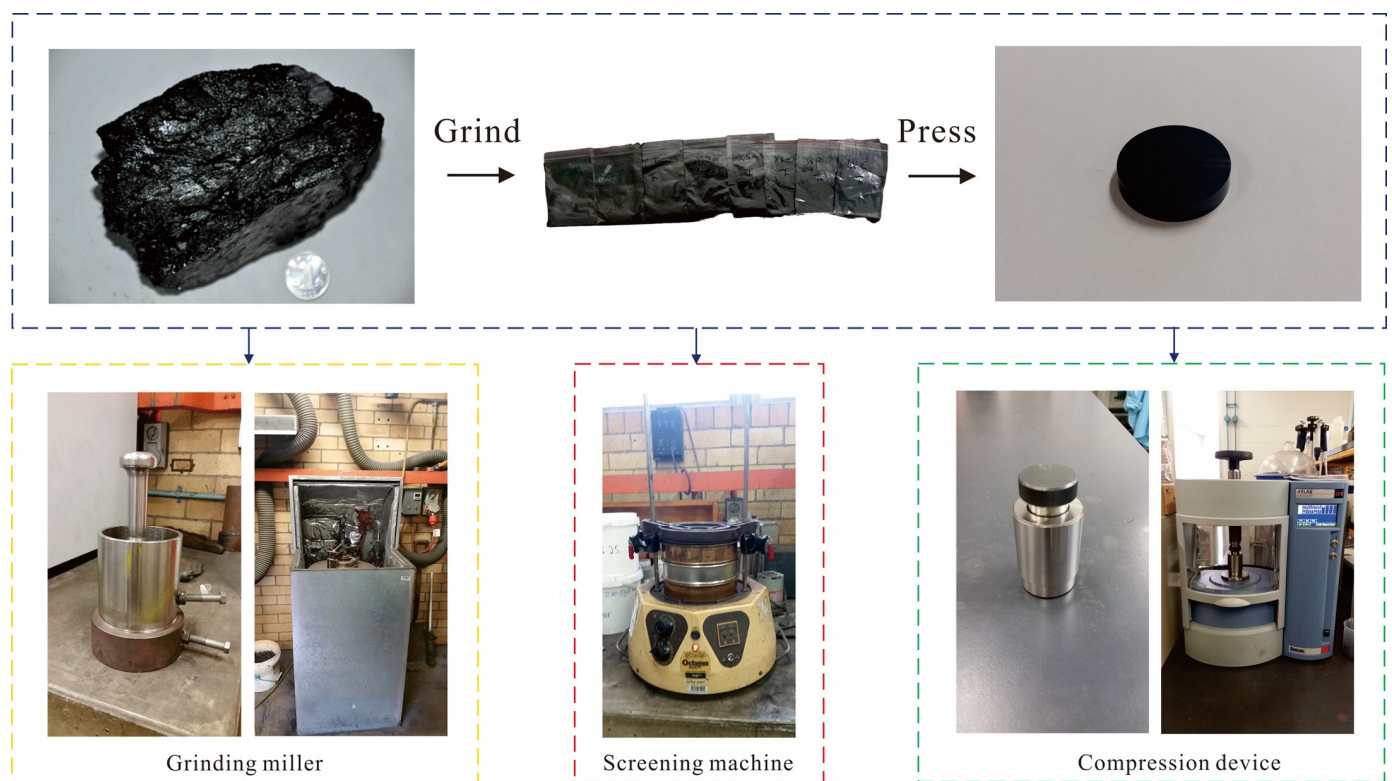
2.1. Sample Collection and Preparation

All coal samples were obtained from three mine sites: Feng Jia Ta, Tai Tou, and Qin Cheng. The FJT and TT samples were collected from the Feng Jia Ta and Tai Tou coal mine, respectively, which are located in the eastern margin of the Ordos basin. QC samples were collected from the Qin Cheng coal mine, which is located in the Qinshui basin. After collection, all the samples were immediately stored in plastic bags to minimize contamination and oxidation. The samples were sent to the laboratory as soon as they were taken out to prevent oxidation of the samples. The maximum vitrinite reflectance (R_o , max), maceral composition content, and proximate analysis are given in Table 1.

Table 1. Information of coal samples including R_o , max, maceral composition, and proximate analysis.

Sample	R_o , Max (%)	Maceral Composition (vol, %)			Proximate Analysis (wt, %)		
		Vitrinite	Inertinite	Minerals	Moisture	Ash	Volatile
FJT	0.68	47.2	38.2	9.7	4.8	12.4	30.6
TT	1.51	70.9	21.9	0	0.8	9.8	19.6
QC	3.02	57.1	35.1	0	3.1	13.9	8.2

In order to minimize the effect of coal surface roughness on wettability, pressed coal samples which had a smoother surface were used in the experiment. All of the raw coal samples were crushed into pulverized coal. Then, the pulverized coal was put through a $212\ \mu\text{m}$ sieve. The pulverized coal samples were put into a dryer for 2 h at $50\ ^\circ\text{C}$. Then, the pulverized coal samples were compressed with a compression device. Five grams of the pulverized coal samples were put into the compression device. The pressure was held at 12 tonnes for 5 min and then relaxed to 6 tonnes. After relaxation, the pressure was held at 10 tonnes for 3 min. Then, the pressed coal samples were taken out and put into a fresh-keeping bag. To prevent the coal samples from being oxidized, all samples were stored in a refrigerator at $-10\ ^\circ\text{C}$ (Figure 1).

**Figure 1.** Sample preparation process and equipment.

2.2. Contact Angle Measurement

Sessile drop contact angles of water in air on the pressed coal samples were measured using a goniometer, which uses a 3 megapixel CMOS digital camera with a 50 mm Nikon lens and a 12 V light source. A volume of $10\ \mu\text{L}$ of deionized water was dripped onto the surface of the pressed coal samples using a Gilson Distriman pipette. Contact angles were measured at five points on each pressed coal sample. The droplet profile images were analyzed using the Image J software (1.46r) using the snake analysis method.

2.3. Gas–Water Flow Experiment

The flow of air and water in the pressed channels was observed in a microfracture flow device (Figure 2). The microfracture flow device consisted of the pressed coal samples, 1.5 mm inlet and outlet holes, Tygon tubing, and 2 mL syringes (Cole Parmer Model 74905-52) for water and air injection. The top of the coal channel was sealed with a polyolefin film. The experiments were performed by the injection of water containing 0.1 wt% fluorescein acid yellow 73 at a rate of 20 $\mu\text{L}/\text{min}$ into the pressed channels. The pressure drop across the channel was measured with a Dwyer Series 490 wet/wet handheld digital manometer. Optical images were collected with a Leica DM6000 light microscope equipped with a Leica DFC365 FX digital high-speed camera. Image analysis was performed with the Leica Application Suite Advanced Fluorescence software package and the ImageJ software, version 1.46r.

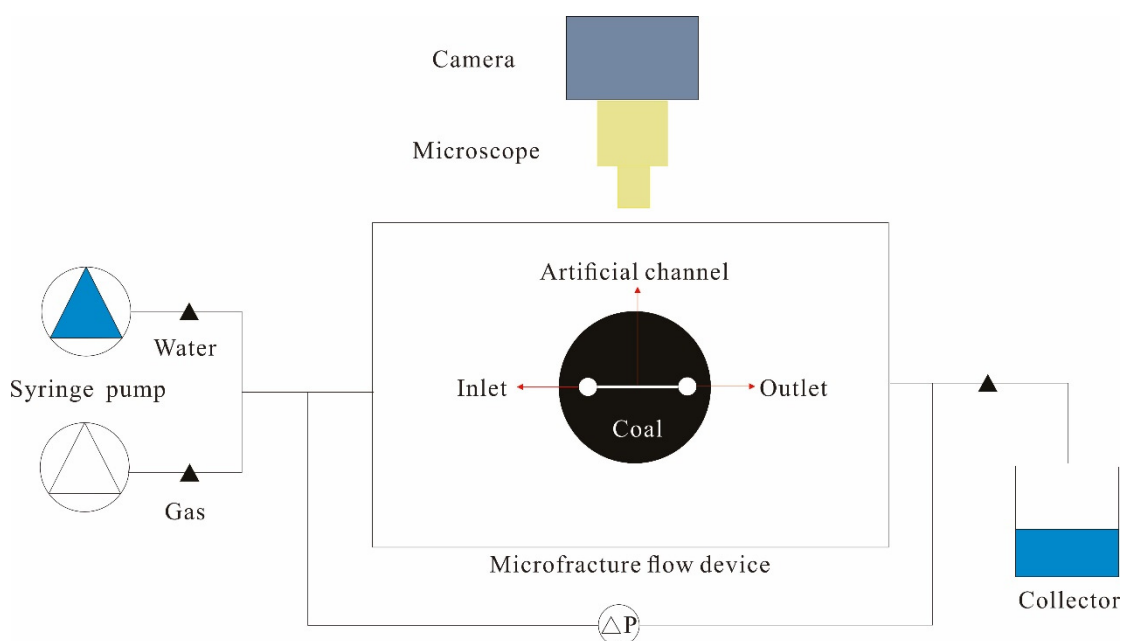


Figure 2. Schematic of the flow experiment apparatus.

2.4. Chemical Treatment of Samples

(1) SiO_2 : Solutions of 100 mL, containing 1% (mass fraction) of SiO_2 , were prepared using deionized water and installed in a 250 mL glassware. Due to the nanoparticles in the SiO_2 solution easily forming aggregates, the solutions were sonicated for 20 min to help separate the nanoparticles in the solutions. The coal disc samples mentioned previously were immersed in the 100 mL 1% SiO_2 solutions for 20 min. Then, the samples were removed and dried in an oven for 2 h at 50 $^{\circ}\text{C}$.

(2) H_2O_2 : A 15% H_2O_2 solution was used in this experiment. Three 3 g samples of coal powder of FJT, TT, and QC were immersed in 20 mL of 15% H_2O_2 . The powdered coal samples were mixed thoroughly with the H_2O_2 solution for 30 min. The pulverized coal samples were then filtered and dried at 50 $^{\circ}\text{C}$ for 12 h. These samples were used for XPS analysis. The coal disc samples mentioned previously were immersed in 100 mL of 15% H_2O_2 for 20 min. The samples were then removed and oven dried at 50 $^{\circ}\text{C}$ for 2 h.

(3) DTAB: The cationic surfactant used in this experiment was DTAB (dodecyl trimethyl ammonium bromide), with a mass fraction of 1%. The coal disc samples mentioned previously were immersed in 100 mL of 1% DTAB for 12 h. The samples were then removed and oven dried at 50 $^{\circ}\text{C}$ for 2 h.

3. Results and Discussion

3.1. Characteristics of Coal Surface after Chemical Treatment

Since the purpose of this experiment is to investigate changes in the surface wettability of coal, rather than directly titrating various chemical reagents onto the surface of the coal, the changes in the surface properties of the coal need to be detected after chemical treatment.

3.1.1. Characteristics of Coal Surface after SiO₂ Treatment

A layer of nanoscale particles adhered to the surface of the coal samples after being treated with SiO₂ solution, indicating that SiO₂ particles had already adhered to the surface. The particle size and aggregation of SiO₂ particles were generally consistent with the research results of Esfandayari et al. [37]. The particle size test of the SiO₂ solution also proves that it will agglomerate (Table 2). According to Riddick et al.'s research, the size of SiO₂ particles adhering to the surface of coal may be related to the concentration of the SiO₂ solution. Despite partial aggregation of SiO₂ particles, SiO₂ particles still adhered to the surface of the coal samples. The particle size of the SiO₂ in the solutions was measured using a Malvern laser particle size tester to investigate the quality dispersion of SiO₂ particles in the solutions. It can be seen from Table 2 that although ultrasonic vibration was used to disperse the particles, the SiO₂ particles in the solution still agglomerated, but the degree of particle aggregation had little impact on the experimental results.

Table 2. Comparison of dried SiO₂ particles and SiO₂ particles in solution.

Sample	Dry Particle Size/nm	Surface Area/m ² /g	Mean Particle Size/nm
SiO ₂	12	190–220	450

3.1.2. Characteristics of Coal Surface after H₂O₂ Treatment

It can be seen from Table 3 that the percentage of C and O in the coal samples treated with hydrogen peroxide solutions changed significantly. The C percentage of the coal samples FJT, TT, and QC decreased from 81.41%, 88.75%, and 91.33% to 76.15%, 81.46%, and 86.17%, respectively, after being treated with hydrogen peroxide solution. Meanwhile the O percentage of the coal samples FJT, TT, and QC increased from 10.59%, 4.21%, and 3.21% to 15.93%, 11.24%, and 9.34%, respectively. These results show that the changes in the C and O percentages of coal sample TT are the most obvious among the samples after treatment with hydrogen peroxide. Due to the high proportion of oxygen-containing functional group side chains in low rank coal, the change in the O percentage of coal sample FJT is smaller than that of coal sample TT. However, due to the high degree of metamorphism, the aromatic ring structure of coal sample QC is arranged more densely and regularly, with more stable properties and less change in the carbon to oxygen ratio.

Table 3. Atomic content of coal samples treated with different chemicals.

Sample Code	Atomic Composition (%)					
	C	O	N	Al	Si	Ca
FJT	81.41	10.59	1.44	1.73	3.86	0.97
FJT-H ₂ O ₂	76.15	15.93	2.21	1.25	3.57	0.89
TT	88.75	4.21	1.72	1.36	3.52	0.44
TT-H ₂ O ₂	81.46	11.24	2.06	1.16	3.32	0.76
QC	91.33	3.12	1.51	1.15	1.55	1.34
QC-H ₂ O ₂	86.17	8.34	2.11	1.36	1.26	0.76

Organic oxygen atoms are the most important heteroatoms in coal, and the type and relative content of oxygen-containing functional groups is important information to characterize the surface wettability of coal. Due to the fact that various elements in

coal are related to the presence of oxygen, the XPS O1s spectra cannot reflect the binding modes of C and O in coal. However, the C in coal is closely related to the form of organic oxygen present. Therefore, the XPS C1s spectra were analyzed to reveal the occurrence state of its adjacent oxygen atoms. We performed Gaussian–Lorentz peak fitting on the spectra of coal sample TT, and the results are shown in Figure 3. According to the curve-fitted results of the XPS C1s spectra, it can be seen that the phenolic hydroxyl content of the coal sample treated with hydrogen peroxide has increased. The increase in the C=O structure indicates that treatment with 15% hydrogen peroxide may lead to an increase in carboxyl and ether functional groups. According to Liu et al.'s research [37], after treatment with a low-concentration hydrogen peroxide solution, electron-rich aromatic rings can be oxidized to produce hydroxyl functional groups; By increasing the concentration of hydrogen peroxide and increasing its oxidizing properties, carboxyl functional groups or aldehyde functional groups can be generated. In this experiment, due to the increase in hydrophilic oxygen-containing functional groups such as hydroxyl groups, it can be determined that the hydrophilicity of the coal samples treated with hydrogen peroxide is enhanced.

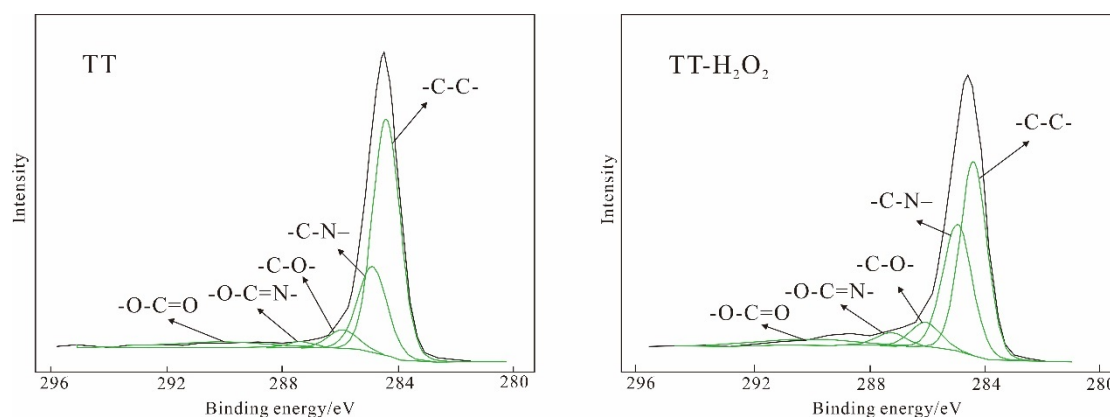


Figure 3. High resolution C1s spectra of the coal samples.

3.2. Alteration of Wettability after Chemical Treatment

The coal samples FJT, TT, and QC were not treated with any chemical treatment, and these coal samples served as a control group to determine the variation in wettability after chemical treatment. Table 4 shows the contact angle measurement results and Figure 4 shows the droplet profiles of each group of samples. Both the SiO₂- and H₂O₂-treated coal samples showed a more spread out drop profile. This means that the contact angles were lower compared to the untreated coal sample. This indicates that a more hydrophilic surface was formed after being treated with SiO₂ and H₂O₂. However, the changes in wettability among the different rank coal samples are not the same. Even being treated with SiO₂ and H₂O₂, high rank coal still has a relatively large contact angle. However, the mechanism of the change in wettability between SiO₂ and H₂O₂ is different. This is because the SiO₂ particles are poorly dispersed on the coal surface. The particles do not completely cover the surface of the coal sample, resulting in a relatively large contact angle. However, H₂O₂ increases the wettability by increasing hydrophilic oxygen-containing functional groups. However, there are few oxygen-containing functional groups in high rank coal. The coal samples treated with DTAB showed a larger contact angle, which indicates that the treatment resulted in a more hydrophobic surface. The contact angles of samples treated with DTAB are generally greater than 90°. On the whole, due to the aggregation and sedimentation of SiO₂ particles, a uniform wetting surface cannot be produced. In the actual production process, the SiO₂ particles are difficult to dissolve in water, which can cause a blockage of the seepage channel and reduce the absolute permeability of the reservoir. Therefore, H₂O₂ and DTAB are relatively more suitable for practical production applications.

Table 4. Contact angle measurement results.

Sample	Contact Angle/°					Average	Standard Deviations
	1	2	3	4	5		
FJT	44.3	38.1	49.5	49.9	46.9	45.74	4.84
FJT-SiO ₂	36.8	46.3	34.2	37.4	47.5	40.44	6.03
FJT-H ₂ O ₂	36.3	30.9	33.7	32.5	34.6	33.60	2.05
FJT-DTAB	96.3	97.6	103.2	98.7	101.5	99.46	2.84
TT	71.2	71	70.3	59.05	59	66.09	6.46
TT-SiO ₂	47.4	55.2	45.3	51.6	60.1	51.92	5.42
TT-H ₂ O ₂	36.5	37.1	32.3	35.5	37.6	35.80	2.11
TT-DTAB	95.4	100.5	103.2	99.4	97.8	99.26	2.92
QC	93.5	96.6	97.1	106	100.5	98.74	4.76
QC-SiO ₂	71.2	65.4	66.3	75.4	78.4	71.34	5.64
QC-H ₂ O ₂	60.8	60.2	56.4	57.4	56.2	58.20	2.16
QC-DTAB	99.5	103.2	104.6	103.5	98.4	101.84	2.72

**Figure 4.** Contact angles of various chemically treated coal samples.

The wettability alteration mechanism among the three different chemical reagents is different. The molecular structure of SiO₂ is a three-dimensional mesh structure, which has Si and O atoms at the center and apex, respectively. The surfaces of SiO₂ nanoparticles have different and numerous hydroxyl groups. These hydroxyl groups easily form hydrogen bonds with water molecules. Thus, the SiO₂ nanoparticles attached to the coal surface can make the coal surface more hydrophilic. H₂O₂ has strong oxidizing properties. The coal samples treated with H₂O₂ can produce hydroxyl functional groups by oxidation of electron-rich aromatic rings. High concentration hydrogen peroxide can further increase surface polar functional groups, such as carboxyl or aldehyde groups. The polar functional groups can make the coal surface more hydrophilic. DTAB is a cationic surfactant with two

different wetting groups on its surface. The two wetting groups are hydrophilic $N^+(CH_3)_3$ and hydrophobic aliphatic chains. The $N^+(CH_3)_3$ and oxygenated functional groups of coal attract each other. Then, the hydrophobic aliphatic chains of DTAB will be immersed in water.

3.3. The Influence of Coal Wettability on the Gas–Water Flow

3.3.1. The Influence of Wettability on the Gas–Water Interface

Figure 5 shows the gas–water flow state in cleats of different coal samples. The coal sample TT was not treated with any chemical solutions, and TT served as a control to determine the variation in wettability after chemical treatment. It can be seen from Figure 5 and Table 5 that the flow state of two-phase flow in cleats was changed after chemical treatment. Between the unmixed water and gas a meniscus interface was formed in the cleat of sample TT. The direction of the capillary force corresponds to the curvature of the interface. In the cleat of TT, the direction of the capillary force was opposite to the flow direction, which means that the cleat surface was hydrophobic. At this point, the capillary force is resistant to water flow. When in equilibrium, the capillary force is equal to the driving force of the water. The coal sample TT-SiO₂ formed different contact angles on the two sides of the cleat (left above 90° and right below 90°). This is because the nanoparticles cannot be evenly dispersed on the surface of the coal cleat. The right gas–water interface is exposed to a concentration sufficient to affect wetting, while the left gas–water interface is directly exposed to the coal matrix. In the cleat of sample TT-H₂O₂, a meniscus interface was formed and the direction of the capillary force corresponded to the water flow. This indicates that the cleat surface transformed from being hydrophobic to hydrophilic after treatment with H₂O₂. In this state, water can more easily migrate through the cleats. In the cleat of sample TT-DTAB, a meniscus interface was formed and the direction of the capillary force corresponds to TT, which indicates that a hydrophobic surface was formed. However, the interface morphology of TT-DTAB is sharper than that of TT. This indicates that compared to TT, the surface hydrophobicity of TT-DTAB is enhanced. Moreover, the capillary force has increased, which means that water finds it more difficult to migrate through the cleats.

Table 5. Parameters in the injection process.

Sample	Pressure Drop/kPa	Injection Rate/ μ L/min	Contact Angle/ $^{\circ}$		Average
			Left	Right	
TT	3.3	10	122.1	124.1	123.1
TT-SiO ₂	1.8	10	123.6	87.8	105.7
TT-H ₂ O ₂	0	10	87.7	77.3	82.5
TT-DTAB	4.6	10	136.2	146.5	141.35

3.3.2. The Influence of Wettability on Gas–Water Flow State

Figure 6 shows that there are two types of gas–water flow patterns during the experiment. When the two-phase flow flowed in the cleat of sample TT-DTAB, a slug flow was formed. There was no water adhering to the cleat surface of the coal when the water flowed through the cleat. Only when all the water had flowed through the cleat would gas gradually be produced. This indicates that on the surface of hydrophobic coal, water did not easily adhere to the coal's surface. Gas can only migrate in the cleat after the water is released. In the CBM drainage process, this type of coal surface has strong hydrophobicity. Water in pores and cleats flows more easily compared to hydrophilic surfaces, resulting in a decrease in the residual water saturation in the reservoir. In the gas production stage, hydrophobic surfaces are more conducive to increasing gas production.

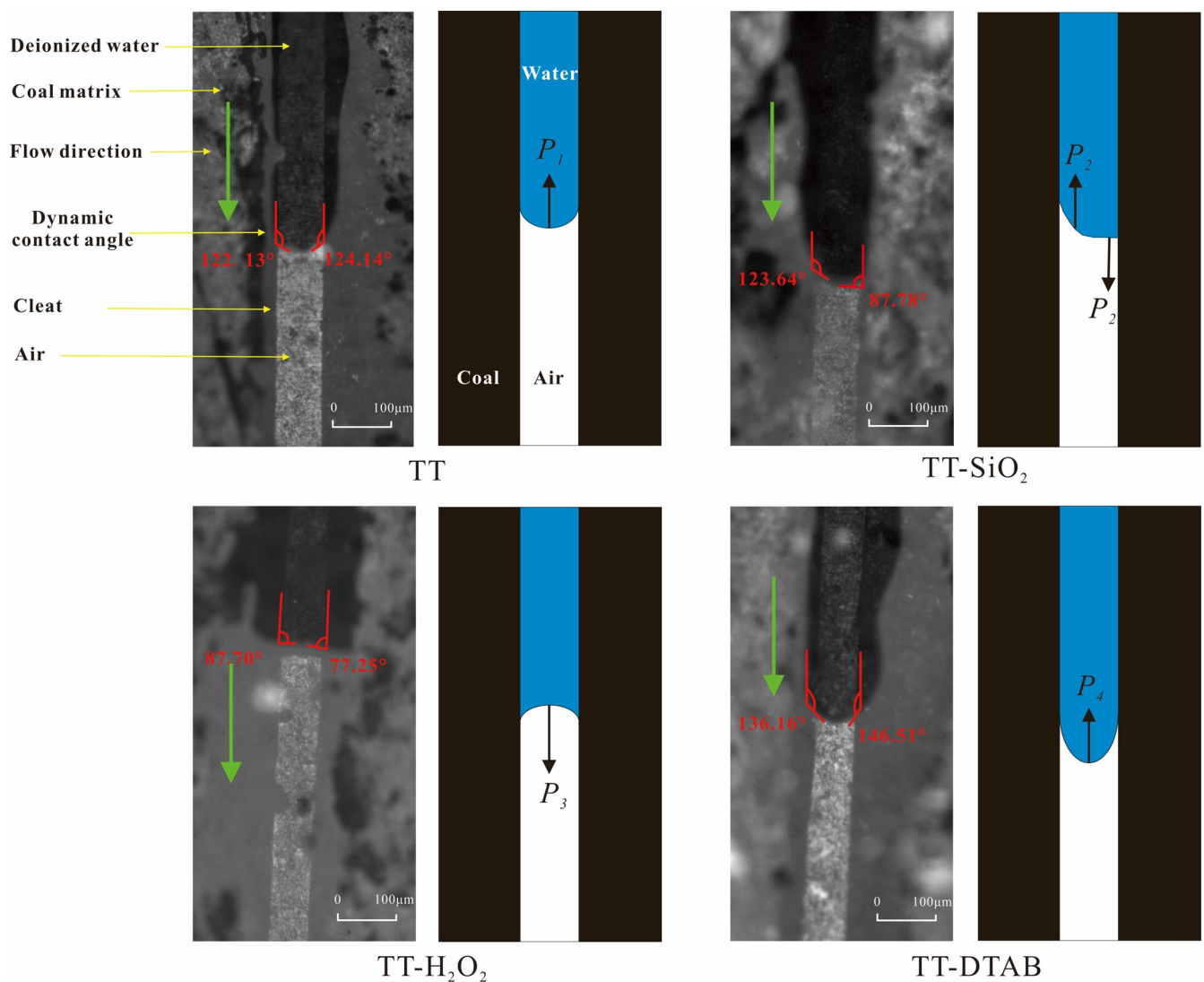


Figure 5. Characteristics of gas–water interface after chemical treatment.

When the two-phase flow flowed in the cleat of sample TT-H₂O₂, an annular flow was formed. A thick water film remained on the surface of the coal, and the residual water film showed a lasting residence time in the coal. After increasing the displacement pressure of gas, the residual water film did not significantly decrease. This indicates that due to the enhanced wettability of the coal surface, the water is more likely to adhere to the surface of the coal, which formed a thick water film. At this point, the gas flow was not affected, but flowed through the middle of the water film and migrated in the seepage channel. The water adhered to the cleat surface and flowed slowly along it. Although the surface of coal is hydrophilic, the water does not occupy the entire seepage channel. Gas can flow through the middle of the water, forming a circular flow, and moving together with the water in the seepage channel. The results of this experiment are consistent with the predictions made by Cubaud et al. in previous studies, as compared to spherical flows formed on hydrophobic surfaces, hydrophilic surfaces are more likely to form annular flows [38]. At this point, the effective permeability of both gas and water increases. In the CBM drainage process, this two-phase flow state can increase the gas relative permeability, which increases the gas production.

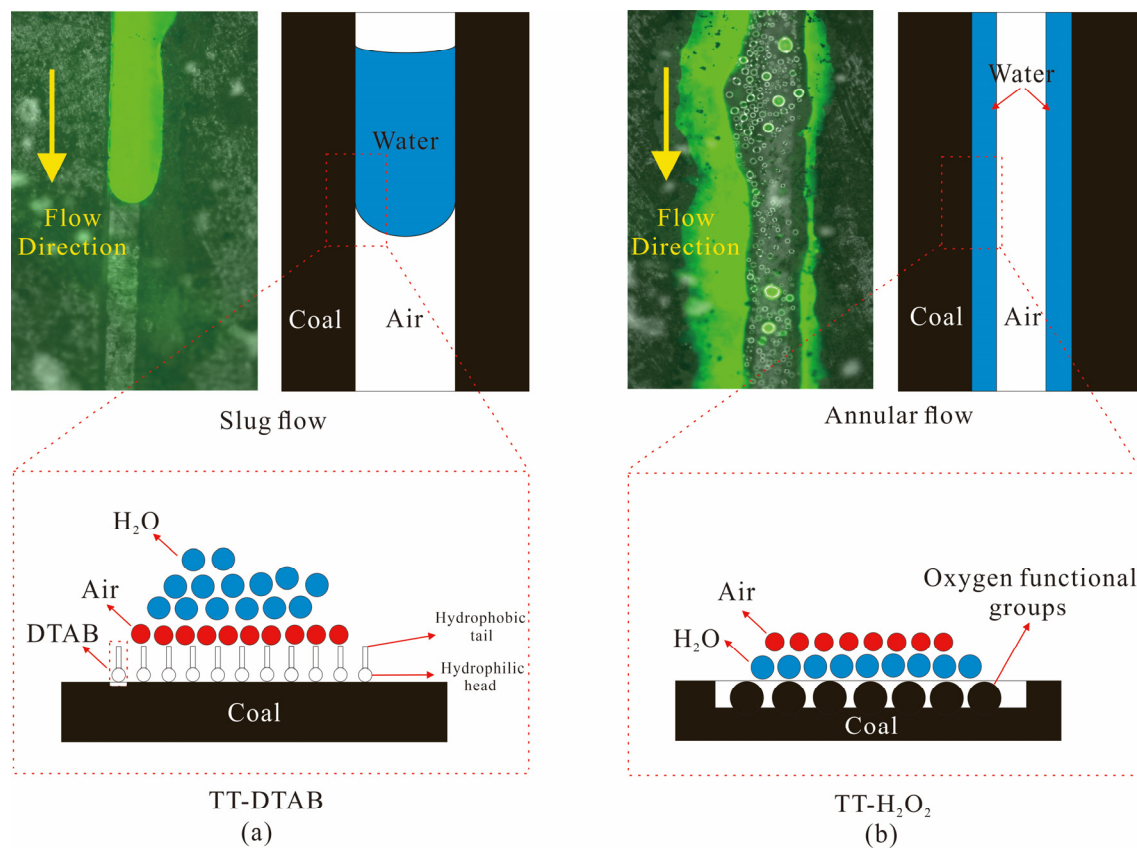


Figure 6. The gas–water flow state. (a) Slug flow; (b) annular flow.

In the micron channel, gas–water flow states are very sensitive to surface wettability and have a significant impact on the actual production of coalbed methane. On a hydrophilic surface, water flows easily through the channels. This will result in more efficient drainage of coalbed methane during the dewatering stage, and the water retention will be reduced. On a hydrophobic surface, water does not easily adhere to the surface of the coal. Thus, the water blockage will be reduced and the gas will easily flow through the channels. In the gas production stage of coalbed methane, hydrophobic surfaces are more favorable to coalbed methane production.

3.4. Relationship between Coal Wettability and Water States

Figure 7a shows several occurrence states of water in cleats. In CBM reservoirs, the occurrence state of water depends on the pore and cleat morphology and coal wettability. However, the distribution of functional groups on the coal surface is the main factor controlling coal wettability.

Figure 7b shows that a thick water film adhered to the surface of coal. This type of water is adsorbed, which enhances the irreducible water content. On a hydrophilic surface, multiple layers of water are formed. Physical and chemical adsorption fixes the adsorbed water to the surface, which is different from gas adsorption [39]. The adsorption capacity of water molecules is higher than that of methane. Hydrogen bonding, which depends on the relative moisture pressure, fixes water molecules on the coal surface [40]. Outside the coal surface, long-range intermolecular forces controlled by the concentration of hydrophilic functional groups hold water molecules in place [41].

Figure 7c shows the bulk water in the cleat. The wettability of coal determines the amount of water molecules adsorbed. Due to the strong hydrophilicity of the coal surface, more and more water molecules are adsorbed on the surface, forming a multi-layer film. As the water content increases, the adsorbed water will transform into bulk water. When the gas pressure increases, this part of the water will be driven away by the gas.

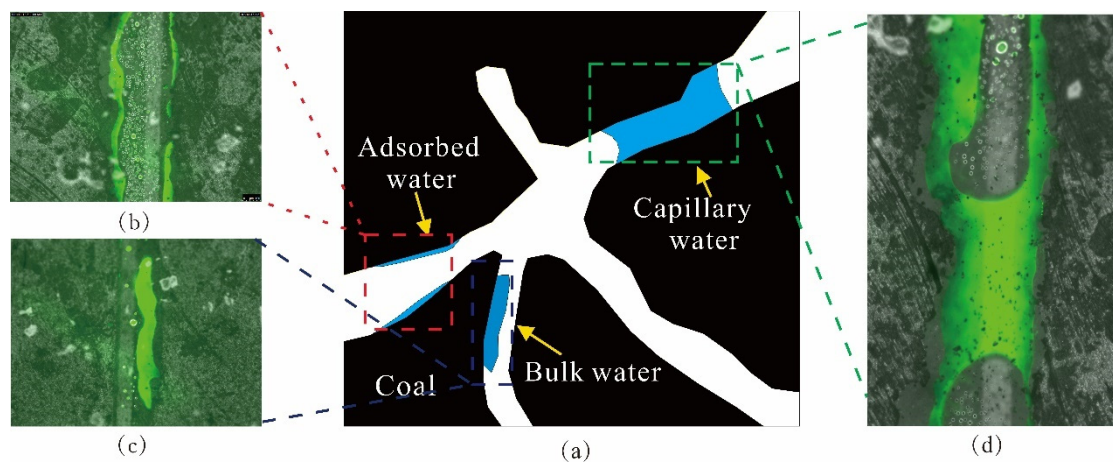


Figure 7. The forms of water present in cleats. (a) Schematic of distribution of adsorbed water, bulk water, and capillary water in the cleats; (b) adsorbed water observed in experiment; (c) bulk water observed in experiment; (d) capillary water observed in experiment.

Figure 7d shows that the contact angle is less than 90° and water is preferentially attracted to the hydrophilic surface. A capillary force is directed towards the gas phase. The direction of the capillary force is opposite to the gas pressure, which hinders the movement of water. As a result, the hydrophilic parts have a higher irreducible water content. Under static conditions, the resultant capillary force is smaller because the direction of the two capillary forces is opposite at the two interfaces. However, when the capillary water is pushed forward, the resultant force changes. This resultant force will hinder the movement of the water.

3.5. The Influence of Coal Wettability on Relative Permeability

Figure 8 shows the relative permeability curves of coal samples with different chemical treatments measured using the steady-state method. It can be seen from Figure 8 that the coal samples treated with H_2O_2 have higher crossover points compared to the untreated coal samples. However, the coal samples treated with DTAB have a lower crossover point compared to the untreated coal samples. The water saturation at the crossover point of coal sample TT- H_2O_2 is 0.63, and the gas–water relative permeability at the crossover point is 0.49. The water saturation at the crossover point of the coal sample TT is 0.58, and the gas–water relative permeability at the crossover point is 0.23. The water saturation at the crossover point of the coal sample TT-DTAB is 0.49, and the gas–water relative permeability at the crossover point is 0.38. The change in the relative permeability curve of TT- H_2O_2 is due to the coal sample TT- H_2O_2 forming a more hydrophilic surface. According to the conclusions in the previous sections, it is easier for the fluid to form a water film on the surface of coal with strong hydrophilicity. This means that a hydrophilic surface on coal samples is formed, which creates an annular flow in the channel. At the same time, gas is more easily transported in the annular flow formed by the water phase, which makes gas migration easier in the seepage channel. The relative permeability curve of TT- H_2O_2 shows that the effective permeability of gas and water increases with the increase in coal surface wettability. By comparing the residual water saturation of TT and TT- H_2O_2 , it can be seen that the residual water saturation of TT- H_2O_2 is higher than TT. However, the TT-DTAB relative permeability curve has a leftward shift from the TT curve, and the residual water saturation is also reduced. This indicates that TT-DTAB formed a more hydrophobic surface. The results show that a hydrophobic surface on TT-DTAB is formed, which creates a globular flow in the channel. This indicates that water in pores and cleats is more easily displaced in a hydrophilic seepage system.

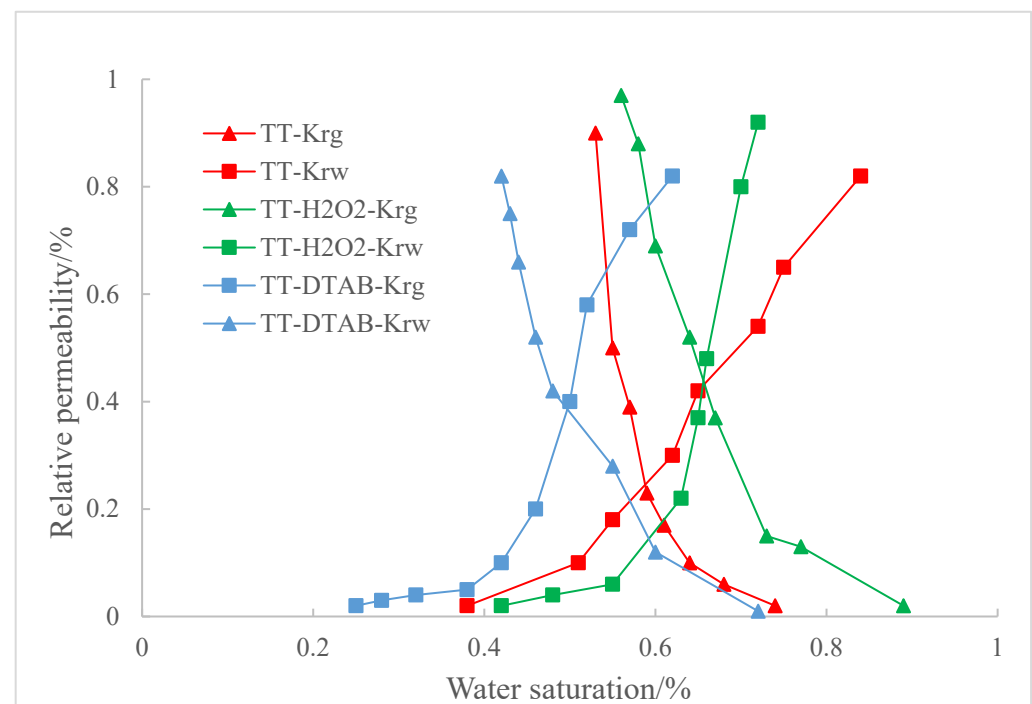


Figure 8. Relative permeability of untreated coal and chemically treated coal samples.

4. Conclusions

(1) The coal samples treated with SiO_2 and H_2O_2 showed an increase in the hydrophilicity of the coal surface, while the coal samples treated with DTAB showed an increase in the hydrophobicity of the coal surface. SiO_2 , H_2O_2 , and DTAB have different mechanisms for changing the wettability.

(2) The direction of the capillary force is the same as the water flow in a hydrophilic surface, while the direction of the capillary force is opposite to the water flow.

(3) There are two types of flow states of gas and water on different wetting surfaces. A slug flow is formed on a hydrophilic surface, while an annular flow is formed on a hydrophobic surface. There are three types of occurrence states under different wetting state: adsorbed water, bulk water, and capillary water.

(4) The relative permeability is influenced by the wetting states of the cleat surface. The residual water saturation increases with the increase in hydrophilicity. The gas–water relative permeability at the crossover point increases after wettability alteration.

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Nomenclature

CBM	Coalbed methane
FJT	Code of coal samples from Feng Jia Ta mine
TT	Code of coal samples from Tai Tou mine
QC	Code of coal samples from Qin Cheng
SiO ₂	Silicon dioxide
H ₂ O ₂	Hydrogen peroxide
DTAB	Dodecyl trimethyl ammonium bromide
FJT-SiO ₂	Sample FJT treated with silicon dioxide
TT-SiO ₂	Sample TT treated with silicon dioxide
QC-SiO ₂	Sample QC treated with silicon dioxide
FJT-H ₂ O ₂	Sample FJT treated with hydrogen peroxide
TT-H ₂ O ₂	Sample TT treated with hydrogen peroxide
QC-H ₂ O ₂	Sample QC treated with hydrogen peroxide
FJT-DTAB	Sample FJT treated with dodecyl trimethyl ammonium bromide
TT-DTAB	Sample TT treated with dodecyl trimethyl ammonium bromide
QC-DTAB	Sample QC treated with dodecyl trimethyl ammonium bromide
K _{rg}	Relative permeability of the gas
K _{rw}	Relative permeability of the water
P	Capillary force
vol.	Volume fraction
wt.	Mass fraction
R _{o, max}	Maximum reflectance of vitrinite

References

- Xin, F.D.; Xu, H.; Tang, D.Z.; Cao, C. Differences in Accumulation Patterns of Low-Rank Coalbed Methane in China under the Control of the First Coalification Jump. *Fuel* **2022**, *324*, 46–57. [\[CrossRef\]](#)
- Liu, D.M.; Jia, Q.F.; Cai, Y.D.; Gao, C.J.; Qiu, F.; Zhao, Z.; Chen, S.Y. A New Insight into Coalbed Methane Occurrence and Accumulation in the Qinshui Basin, China. *Gondwana Res.* **2022**, *111*, 280–297. [\[CrossRef\]](#)
- Shuxun, S.; Sijie, H.; Shiqi, L.; Xiaozhi, Z.; Mengxi, L.; Qiujia, H.; Cong, Z. Comprehensive Study on the Enrichment Mechanism of Coalbed Methane in High Rank Coal Reservoirs. *J. China Coal Soc.* **2022**, *47*, 388–403.
- Tao, S.; Pan, Z.J.; Tang, S.L.; Chen, S.D. Current Status and Geological Conditions for the Applicability of CBM Drilling Technologies in China: A Review. *Int. J. Coal Geol.* **2019**, *202*, 95–108. [\[CrossRef\]](#)
- Wu, Y.N.; Tao, S.; Tian, W.G.; Chen, H.; Chen, S.D. Advantageous Seepage Channel in Coal Seam and Its Effects on the Distribution of High-Yield Areas in the Fanzhuang CBM Block, Southern Qinshui Basin, China. *Nat. Resour. Res.* **2021**, *30*, 2361–2376. [\[CrossRef\]](#)
- Dutka, B. Effect of Depth on the Sorption Capacity of Coals Affected by Outburst Hazard. *Fuel* **2021**, *306*, 121611. [\[CrossRef\]](#)
- Shu, L.Y.; Wang, K.; Liu, Z.S.; Zhao, W.; Zhu, N.N.; Lei, Y. A Novel Physical Model of Coal and Gas Outbursts Mechanism: Insights into the Process and Initiation Criterion of Outbursts. *Fuel* **2022**, *323*, 124305. [\[CrossRef\]](#)
- Crow, D.J.G.; Giarola, S.; Hawkes, A.D. A Dynamic Model of Global Natural Gas Supply. *Appl. Energy* **2018**, *218*, 452–469. [\[CrossRef\]](#)
- Qin, Y.; Moore, T.A.; Shen, J.; Yang, Z.B.; Shen, Y.L.; Wang, G. Resources and Geology of Coalbed Methane in China: A Review. *Int. Geol. Rev.* **2018**, *60*, 777–812. [\[CrossRef\]](#)
- Wang, Z.W.; Liu, S.M.; Qin, Y. Coal Wettability in Coalbed Methane Production: A Critical Review. *Fuel* **2021**, *303*, 121277. [\[CrossRef\]](#)
- Shen, J.; Qin, Y.; Wang, G.X.; Fu, X.H.; Wei, C.T.; Lei, B. Relative Permeabilities of Gas and Water for Different Rank Coals. *Int. J. Coal Geol.* **2011**, *86*, 266–275. [\[CrossRef\]](#)
- Clarkson, C.R. Production Data Analysis of Unconventional Gas Wells: Review of Theory and Best Practices. *Int. J. Coal Geol.* **2013**, *109*, 101–146. [\[CrossRef\]](#)
- Ofori, P.; Firth, B.; O'Brien, G.; McNally, C.; Nguyen, A.V. Assessing the Hydrophobicity of Petrographically Heterogeneous Coal Surfaces. *Energy Fuels* **2010**, *24*, 5965–5971. [\[CrossRef\]](#)
- Gosiewska, A.; Drelich, J.; Laskowski, J.S.; Pawlik, M. Mineral Matter Distribution on Coal Surface and Its Effect on Coal Wettability. *J. Colloid Interface Sci.* **2002**, *247*, 107–116. [\[CrossRef\]](#)
- Susana, L.; Campaci, F.; Santomaso, A.C. Wettability of Mineral and Metallic Powders: Applicability and Limitations of Sessile Drop Method and Washburn's Technique. *Powder Technol.* **2012**, *226*, 68–77. [\[CrossRef\]](#)
- Li, Q.Z.; Lin, B.Q.; Zhao, S.; Dai, H.M. Surface Physical Properties and Its Effects on the Wetting Behaviors of Respirable Coal Mine Dust. *Powder Technol.* **2013**, *233*, 137–145. [\[CrossRef\]](#)

17. Ibrahim, A.F.; Nasr-El-Din, H.A. Effects of Formation-Water Salinity, Formation Pressure, Gas Composition, and Gas-Flow Rate on Carbon Dioxide Sequestration in Coal Formations. *SPE J.* **2017**, *22*, 1530–1541. [\[CrossRef\]](#)
18. Wang, X.; Qu, Z.; Ren, G. Collective Enhancement in Hydrophobicity and Electrical Conductivity of Gas Diffusion Layer and the Electrochemical Performance of PEMFCs. *J. Power Sources* **2023**, *575*, 233077. [\[CrossRef\]](#)
19. Zhang, J.Y.; Feng, Q.H.; Zhang, X.M.; Wen, S.M.; Zhai, Y.Y. Relative Permeability of Coal: A Review. *Transp. Porous Media* **2015**, *106*, 563–594. [\[CrossRef\]](#)
20. Mahoney, S.A.; Rufford, T.E.; Johnson, D.; Dmyterko, A.S.K.; Rodrigues, S.; Esterle, J.; Rudolph, V.; Steel, K.M. The Effect of Rank, Lithotype and Roughness on Contact Angle Measurements in Coal Cleats. *Int. J. Coal Geol.* **2017**, *179*, 302–315. [\[CrossRef\]](#)
21. Chen, Y.X.; Liu, D.M.; Yao, Y.B.; Cai, Y.D.; Chen, L.W. Dynamic Permeability Change during Coalbed Methane Production and Its Controlling Factors. *J. Nat. Gas Sci. Eng.* **2015**, *25*, 335–346. [\[CrossRef\]](#)
22. Mchirgui, W.; Millet, O.; Amiri, O. Theoretical Study and Simulation of Moisture Transport in Unsaturated Porous Media by Periodic Homogenization. *Int. J. Numer. Anal. Methods Geomech.* **2015**, *39*, 409–435. [\[CrossRef\]](#)
23. Chen, D.; Pan, Z.J.; Liu, J.S.; Connell, L.D. Modeling and Simulation of Moisture Effect on Gas Storage and Transport in Coal Seams. *Energy Fuels* **2012**, *26*, 1695–1706. [\[CrossRef\]](#)
24. Teng, T.; Wang, J.G.; Gao, F.; Ju, Y.; Xia, T.Q. Impact of Water Film Evaporation on Gas Transport Property in Fractured Wet Coal Seams. *Transp. Porous Media* **2016**, *113*, 357–382. [\[CrossRef\]](#)
25. Karimi, A.; Fakhroueian, Z.; Bahramian, A.; Khiabani, N.P.; Darabad, J.B.; Azin, R.; Arya, S. Wettability Alteration in Carbonates Using Zirconium Oxide Nanofluids: EOR Implications. *Energy Fuels* **2012**, *26*, 1028–1036. [\[CrossRef\]](#)
26. Kilau, H.W.; Pahlman, J.E. Coal wetting ability of surfactant solutions and the effect of multivalent anion additions. *Colloids Surf.* **1987**, *26*, 217–242. [\[CrossRef\]](#)
27. Naik, S.; You, Z.; Bedrikovetsky, P. Effect of Wettability Alteration on Productivity Enhancement in Unconventional Gas Reservoirs: Application of Nanotechnology. In Proceedings of the Society of Petroleum Engineers—SPE Asia Pacific Unconventional Resources Conference and Exhibition, Brisbane, Australia, 9–11 November 2015. [\[CrossRef\]](#)
28. Wang, G.D.; Ren, T.; Wang, K.; Zhou, A.T. Improved Apparent Permeability Models of Gas Flow in Coal with Klinkenberg Effect. *Fuel* **2014**, *128*, 53–61. [\[CrossRef\]](#)
29. Si, L.L.; Li, Z.H.; Yang, Y.L. Evolution Characteristics of Gas Permeability Under Multiple Factors. *Transp. Porous Media* **2019**, *127*, 415–432. [\[CrossRef\]](#)
30. Edalatpour, M.; Liu, L.; Jacobi, A.M.; Eid, K.F.; Sommer, A.D. Managing Water on Heat Transfer Surfaces: A Critical Review of Techniques to Modify Surface Wettability for Applications with Condensation or Evaporation. *Appl. Energy* **2018**, *222*, 967–992. [\[CrossRef\]](#)
31. Shen, J.; Qin, Y.; Li, Y.P.; Wang, G. Experimental Investigation into the Relative Permeability of Gas and Water in Low-Rank Coal. *J. Pet. Sci. Eng.* **2019**, *175*, 303–316. [\[CrossRef\]](#)
32. Liu, Z.X.; Liu, Z.C.; Zong, Z.M.; Wei, X.Y.; Wang, J.; Lee, C.W. GC/MS Analysis of Water-Soluble Products from the Mild Oxidation of Longkou Brown Coal with H₂O₂. *Energy Fuels* **2003**, *17*, 424–426. [\[CrossRef\]](#)
33. Liu, F.J.; Wei, X.Y.; Zhu, Y.; Wang, Y.G.; Li, P.; Fan, X.; Zhao, Y.P.; Zong, Z.M.; Zhao, W.; Wei, Y.B. Oxidation of Shengli Lignite with Aqueous Sodium Hypochlorite Promoted by Pretreatment with Aqueous Hydrogen Peroxide. *Fuel* **2013**, *111*, 211–215. [\[CrossRef\]](#)
34. Fuerstenau, D.W.; Diao, J.; Williams, M.C. Characterization of the Wettability of Solid Particles by Film Flotation 1. Experimental investigation. *Colloids Surf.* **1991**, *60*, 127–144. [\[CrossRef\]](#)
35. Polat, M.; Polat, H.; Chander, S. Physical and Chemical Interactions in Coal Flotation. *Int. J. Miner. Process.* **2003**, *72*, 199–213. [\[CrossRef\]](#)
36. Sadler, L.Y.; Chang, C. Chemical enhancement of coal seam permeability. *In Situ* **1988**, *12*, 103375.
37. Bayat, A.E.; Junin, R.; Samsuri, A.; Piroozian, A.; Hokmabadi, M. Impact of Metal Oxide Nanoparticles on Enhanced Oil Recovery from Limestone Media at Several Temperatures. *Energy Fuels* **2014**, *28*, 6255–6266. [\[CrossRef\]](#)
38. Cubaud, T.; Ulmanella, U.; Ho, C.M. Two-Phase Flow in Microchannels with Surface Modifications. *Fluid Dyn. Res.* **2006**, *38*, 772–786. [\[CrossRef\]](#)
39. Gautam, S.; Liu, T.T.; Cole, D. Sorption, Structure and Dynamics of CO₂ and Ethane in Silicalite at High Pressure: A Combined Monte Carlo and Molecular Dynamics Simulation Study. *Molecules* **2019**, *24*, 99. [\[CrossRef\]](#)
40. Li, P.; Ma, D.M.; Zhang, J.C.; Tang, X.; Huo, Z.P.; Li, Z.; Liu, J.L. Effect of Wettability on Adsorption and Desorption of Coalbed Methane: A Case Study from Low-Rank Coals in the Southwestern Ordos Basin, China. *Ind. Eng. Chem. Res.* **2018**, *57*, 12003–12015. [\[CrossRef\]](#)
41. Zhou, Y.A.; Sun, W.J.; Chu, W.; Liu, X.Q.; Jing, F.L.; Xue, Y. Theoretical Insight into the Enhanced CH₄ Desorption via H₂O Adsorption on Different Rank Coal Surfaces. *J. Energy Chem.* **2016**, *25*, 677–682. [\[CrossRef\]](#)

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