


Research Article

Study on H₂S Occurrence in Low Sulfur Coal Seams

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Coal samples from the Shanxi Shaping coal mine were selected to investigate the occurrence of H₂S in low sulfur coal seams. The adsorption mechanism of coal to H₂S was explored, and an occurrence equation for H₂S in coal seams was fitted through adsorption experiment results. The results showed that under ambient temperature and pressure conditions, the H₂S adsorbed by coal reached equilibrium within 24 h. The increase in H₂S concentrations and the moisture content of coal samples resulted in an increase in the adsorption capacity of H₂S. Chemical adsorption of H₂S by the coal also occurred. The total sulfur content in the coal increased, and water promoted the conversion from H₂S to sulfur in coal. After adsorption, most of the H₂S remains in the coal structure in the form of inorganic sulfur, such as sulfur hydride, iron sulfide sulfur, and monomeric sulfur, and a small proportion of H₂S is bonded in the structure of the coal in the form of organic sulfur such as thiophene, C-S-C, and C-SH. Therefore, the higher the total sulfur content in coal, the greater the occurrence of H₂S. The total amount of H₂S increased exponentially with the concentration of free H₂S and the moisture content of coal at equilibrium. This meant that the total amount of H₂S in the coal seam could be estimated by fitting an equation according to the concentration of free H₂S and the moisture content of coal seams. The concentration of free H₂S decreased linearly with the increase in moisture content of the coal, therefore, the concentration of H₂S in space could be reduced by injecting water into coal seams.

1. Introduction

Hydrogen sulfide (H₂S) is the most common toxic gas found in coal mines [1]. Excessive concentrations of H₂S can cause vital harm, including fatality and the risk of explosion. H₂S reacts readily with metal equipment and causes electrochemical and stress corrosion, hydrogen embrittlement rupture, and other damage, reducing the service life of underground metal equipment. This causes significant safety risks [2, 3]. The Coal Mine Safety Regulations clearly stipulate that the H₂S gas concentration in coal mines should not exceed 6.6 ppm. The content of H₂S in coal seams is an important indicator that can be monitored to prevent H₂S accidents in mines. It is also the basis for selecting treatment methods.

Studies have found that the H₂S content in coal seams is related to the total sulfur content of the coal [4]. In the process of geological evolution, sulfur element has remained in coal seams to form sulfur-containing coal, which can pro-

duce a large amount of H₂S gas through biological sulfate reduction (BSR) and sulfate thermal reduction (TSR) [5–7]. Liu et al. [8] found that sulfate in coal seams could be transformed into organic sulfur and iron sulfide, and H₂S appeared as an intermediate product of this transformation. However, Deng et al. [9] found that due to change in geological conditions, H₂S dissolved in water infiltrated into deeper coal seams and remained in the coal body through a series of physical and chemical reactions. This eventually led to an increase in the total sulfur content in coal. Lin et al. [10] found that the active iron ions in coal react with H₂S to form iron-sulfur compounds, resulting in a higher total sulfur content of the coal seams which contained H₂S. Asaoka et al. [11] found that H₂S would be adsorbed on the coal fly ash of coal seams with a higher oxidation degree, and occurred the redox reaction with that. Most of the H₂S would be oxidized to form elemental sulfur and a small part would be oxidized to form sulfate.

At present, the methods for measuring H_2S in coal seams can be divided into direct and indirect methods [12, 13]. Direct methods involve studying the desorption rule of coal samples and estimating the H_2S content of coal seams by underground drilling. Harvey et al. [14] considered that the H_2S content of coal seams in southern Australia was approximately $4 \times 10^{-2} \text{ m}^3/\text{t}$ from the H_2S content desorbed during mining. Xu [15] analyzed the desorption rule of coal samples by a drilling cutting method, and concluded that the H_2S content in the coal seams of the Gaojiapu mine was approximately $2.704 \times 10^{-3} \text{ m}^3/\text{t}$. Indirect methods estimate the content of H_2S in coal seams by measuring the coal seam pressure, adsorption constant, porosity, and industrial analysis parameters. Gao [16] concluded that the H_2S content in the coal seam of Wudong Mine was $4.57 \times 10^{-4} \text{ m}^3/\text{t}$ through onsite testing of the coal seam pressure, laboratory determination of coal adsorption parameters, and industrial analysis data.

Both direct and indirect methods need to be based on the adsorption data of the coal to H_2S . The research on the adsorption of coalbed methane mainly focuses on the adsorption of multiple mixed gases composed of CO_2 , N_2 , and CH_4 [17–20], but there are few research results on the H_2S adsorption by coal. Lu [21] found that the H_2S adsorption by coal belonged to physical adsorption, and the adsorption capacity of H_2S is greater than that of CH_4 and N_2 . The main factors affecting the adsorption of H_2S by coal are pore, maceral, water, pressure, and coalification degree. Ye et al. [22] studied the adsorption of H_2S by coal via a partial pressure test method, and considered that the adsorption amount of H_2S by coal increased with pressure and decreased with temperature. Cheng et al. [23] concluded that the higher the degree of coal metamorphism, the more favorable the adsorption of H_2S by isothermal adsorption under equilibrium water conditions. Yang et al. [4] used H_2S aqueous solution to soak coal samples and found that the solution created a significant increase in the pore volume of coal. The volume of open pores and semiclosed pores increased, the total pore volume of the coal increased by 23.09%, so the adsorption capacity of the samples increased on the side. At present, research on the adsorption rule change of coal to H_2S only accounts for factors such as pressure, temperature, and the metamorphic degree. The influence of other factors on the adsorption of H_2S by coal has not been included, and research on the adsorption mechanism of coal to H_2S has not been explored in depth. On the other hand, both the direct and indirect methods estimate the total content of H_2S in coal seam which only originates from the content of adsorbed H_2S in coal seam. In addition to the adsorbed state, the occurrence of H_2S in the coal body is also found in the form of free and water-soluble states. Therefore, the current method of measuring the content of H_2S has the disadvantages of difficulty in measurement and low accuracy.

In this paper, a self-made experimental device was used to carry out H_2S adsorption experiment at the atmosphere temperature and pressure. The quantitative influence of the H_2S concentration, and the moisture content of coal, on the adsorption of H_2S by coal was analyzed. The total amount of H_2S in a coal seam can be calculated by measur-

TABLE 1: Industrial analysis and total sulfur content analysis of SP coal.

A_{ad}	Industrial analysis(%)			Total sulfur(%)	
	V_{ad}	M_{ad}	FC_{ad}	$S_{t,d}$	
26.98	25.38	1.9	45.74	0.73	

Note: daf means dry ash-free basis, ad means air-dry basis, A_{ad} -Ash content, V_{ad} -Volatile content, M_{ad} -Moisture, FC_{ad} -Carbon content, $S_{t,d}$ -Total sulfur.

ing the free H_2S concentration and the moisture content of the seam. At the same time, X-ray photoelectron spectroscopy (XPS) were used to analyze changes of sulfur-containing groups in coal before and after H_2S adsorption, to explore the transformation relationship between H_2S and sulfur-containing groups. It is of significant importance that a method of estimating the amount of H_2S in coal seams is outlined, and that a theoretical basis is provided for the prevention and control of H_2S in coal mines.

2. Experiment

2.1. Sample Preparation

2.1.1. Coal Sample Preparation. Experimental coal samples were collected from Shanxi Shaping (SP) Coal Mine, coal seam No.13, which has the H_2S concentration exceedance problem. According to the national standard industrial analysis method of coal (GB/T212-2008) and the standard for the determination method of total sulfur in coal (GB/T214-2007), the industrial and total sulfur content analysis of raw coal were carried out. The results are shown in Table 1. According to the national standard coal quality classification (GB/T15224.2-2021), the sulfur content of SP coal is between 0.5% and 1%, which is low sulfur coal.

SP raw coal was crushed, sieved, and pulverized until a particle size of 60–80 mesh (0.18–0.25 mm) was obtained for the adsorption test. To prevent coal samples from exposure to moisture and possible oxidation, the sieved coal samples were vacuum dried and stored. Five 1 g samples of dry coal were weighed by electronic balance, and four samples were sprayed with 0.031, 0.053, 0.111, and 0.25 g of distilled water, respectively. This method ensured that samples with a water content of 0, 3, 5, 10, and 20% were prepared successfully.

When preparing water-immersed coal samples, 5 g of coal was weighed, and completely immersed in distilled water with a solid-liquid ratio of 1:1. The experiment was carried out after mechanical stirring for 24 h.

2.1.2. Adsorption Gas Preparation. The H_2S used in the experiment was a self-made adsorption gas. To eliminate the interference of other gases on the adsorption of H_2S by coal, the N_2 was used as the background gas. The gasification process is shown in Figure 1. In the experiment, N_2 was used to purge the entire gas system. A certain amount of dilute sulfuric acid and ferrous sulfide were placed in the Kipp's apparatus, and the gas collection bag was opened. The H_2S produced by the reaction was diluted with N_2 and dried. The N_2 flow rate was controlled by a pressure regulator to

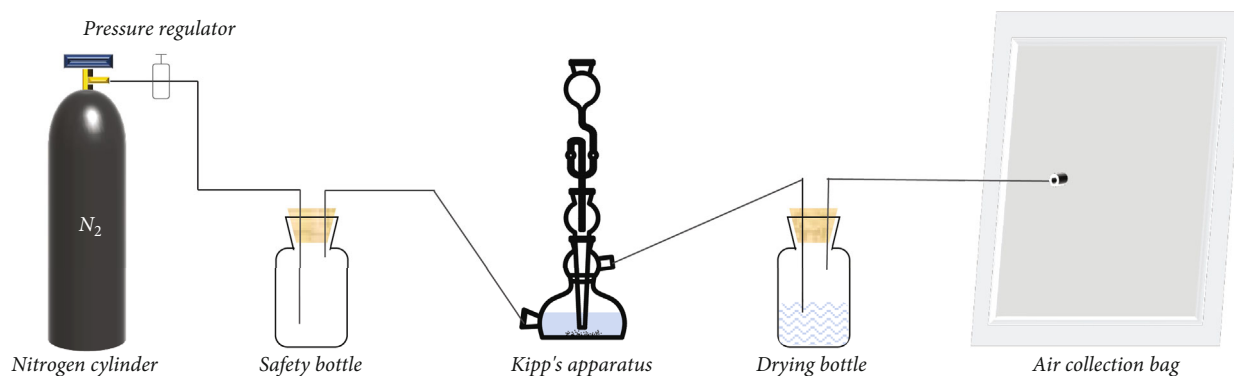
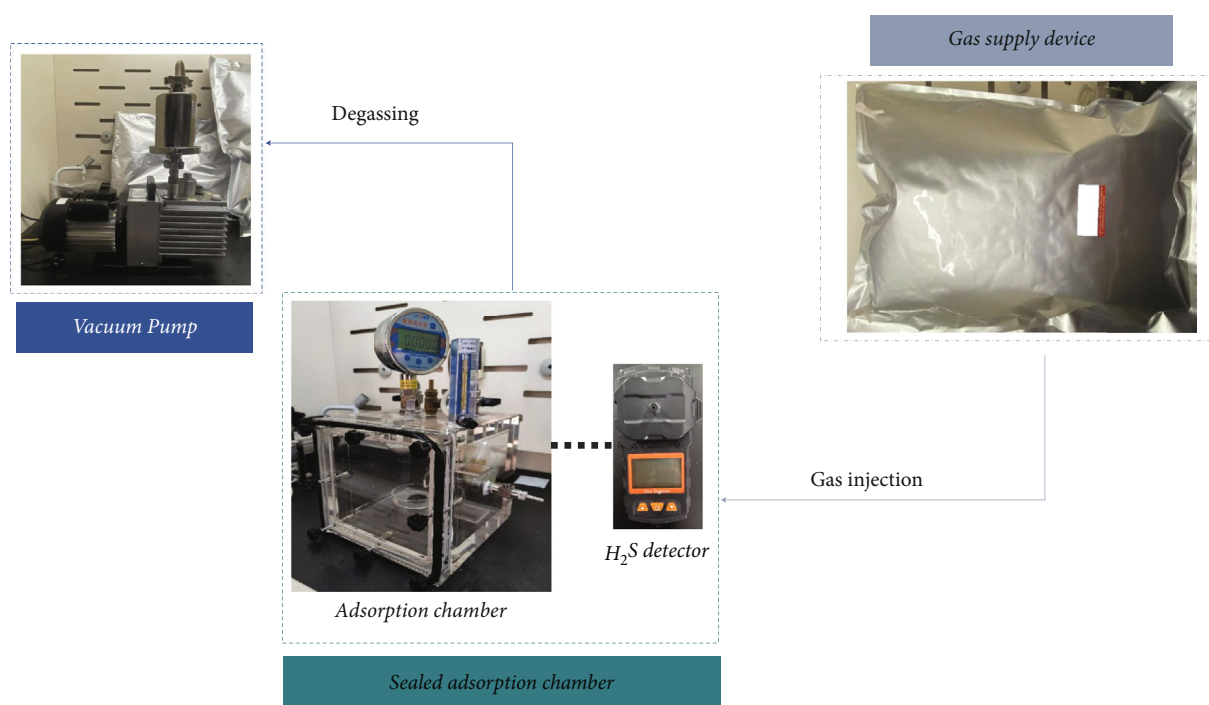


FIGURE 1: Flow diagram of gas production.

FIGURE 2: Experimental system for H_2S adsorption in coal at the atmosphere temperature and pressure (Vacuum Pump, Adsorption chamber, H_2S detector, and H_2S collection bag photograph courtesy of Zhe Jia, Copyright 2022).

control the collected H_2S concentration. H_2S gas mixtures with concentrations of 52, 96, 260, 400, 465, 750, 800, and 860 ppm were prepared.

2.2. H_2S Adsorption Experiment

2.2.1. Experimental System. The coal adsorption H_2S experimental system is shown in Figure 2, including the gas supply device, vacuum pump, and H_2S detector. The gas supply device, the vacuum pump, and the H_2S detector were connected with the sealed adsorption chamber through the pipeline. The adsorption chamber was made of an acrylic material that does not react with H_2S . The adsorption chamber length (l) was 19 cm, width (w) was 19 cm, height (h) was 20 cm, volume:

$$V = lwh = 19 \times 19 \times 20 \text{ cm}^3 = 7.22 \times 10^3 \text{ cm}^3 = 7.22 \text{ L}. \quad (1)$$

After degassing, 400 ppm of H_2S was introduced into the adsorption chamber to a pressure slightly higher than 0.1 MPa. After 24 h, the pressure in the adsorption chamber remained unchanged. The H_2S detector showed that there was no gas leakage outside the adsorption chamber, and the H_2S gas concentration in the adsorption chamber remained at 400 ppm, indicating adsorption chamber was good at air tightness.

2.2.2. Experimental Scheme. To study the effect of the gas concentration on the adsorption of H_2S by coal, the five dry samples were placed in the adsorption chamber. A vacuum pump was used to degas the adsorption chamber over 2 h. Using a gas delivery pump, H_2S was introduced to the adsorption chamber at a pressure 0.1 MPa greater than the existing chamber pressure. This was done for each sample with concentrations of 52, 96, 260, 465, and 850 ppm. The

H₂S concentration in the adsorption chamber was measured by a H₂S detector every 2 h. The pressure of the adsorption chamber and the ambient temperature changes were recorded for 24 h. The adsorption experiments with different H₂S concentrations were sequentially labeled as SP-52, SP-96, SP-260, SP-465, and SP-850.

To study the effect of water content on the adsorption of H₂S by coal, adsorption experiments using 750 ppm H₂S gas and coal samples with a water content of 0, 3, 5, 7, 10, and 20% were carried out in turn. The experimental steps were the same as those above. The adsorption of H₂S by coal samples with different water content was labeled as SP-0%, SP-3%, SP-5%, SP-7%, SP-10%, and SP-20%.

According to the ideal gas equation, the amount of H₂S in the gas phase space of the adsorption chamber at any time during the adsorption process can be calculated:

$$n_i = \frac{P_i V}{RT_i}, \quad (2)$$

where P_i is the partial pressure of H₂S in adsorption chamber (Pa); V is the volume of the adsorption chamber (0.00722 m³); n_i is the amount of substance adsorbing H₂S in the chamber (mol); T_i is the ambient temperature during the adsorption process (K); R is the gas constant of ideal gas, approximately 8.314 J/(mol·K);

$$V_i = \frac{(n_0 - n_i)V_m}{m} \times 10^3, \quad (3)$$

where V_i is the adsorption capacity of coal to H₂S at a certain time point (m³/t); V_m is the molar volume of gas at the atmosphere temperature and pressure (24.5 L/mol); n_0 is the total amount of H₂S in the adsorption chamber (mol); n_i is the amount of free H₂S in the adsorption chamber (mol); m is the mass of coal (g).

2.3. Experiment on the Influence of H₂S Adsorption on Sulfur Forms in Coal. A 5 g dry coal sample, raw coal, and water-immersed coal, use the above adsorption experiment method to adsorb H₂S with a concentration of 400 and 800 ppm, respectively. After adsorption, the adsorbed H₂S was removed by vacuum pump for 2 h. According to the Coulomb titration method, the total sulfur content in coal before and after adsorption of H₂S was analyzed by LCS-430 automatic sulfur analyzer. The sample mass was 50 mg, the catalyst used was tungsten trioxide, and the combustion temperature was 1050°C.

X-ray photoelectron spectroscopy (XPS) technology was used to analyze the morphological changes of sulfur on the coal surface before and after the adsorption of H₂S by using an AXISULTRAD LD instrument from the Kratos Analytical Company. The X-ray source used was Al K α radiation ($h\nu = 1486.6$ eV), and the sample analysis area was 700 × 300 μ m. The measurement parameters were as follows: working power 150 W, full scanning transmittance 160 eV, energy analyzer fixed transmission energy 40 eV, vacuum degree 10⁻⁸ Pa, and step size 0.05 eV. The binding energy correction was per-

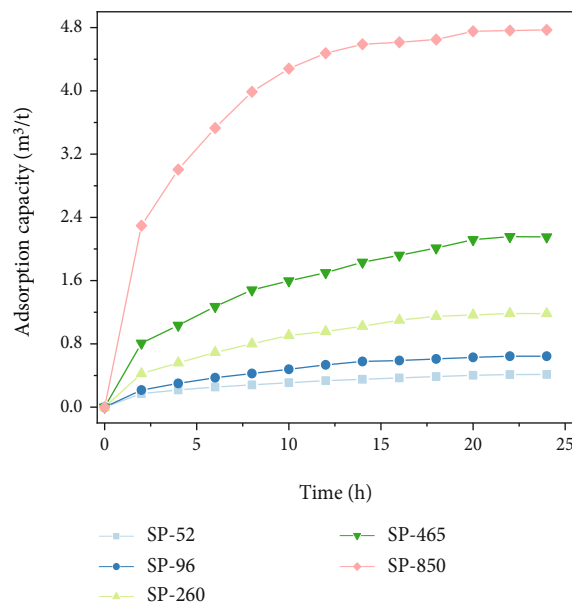


FIGURE 3: Variation curve of amount of H₂S adsorbed over time for different concentrations of H₂S.

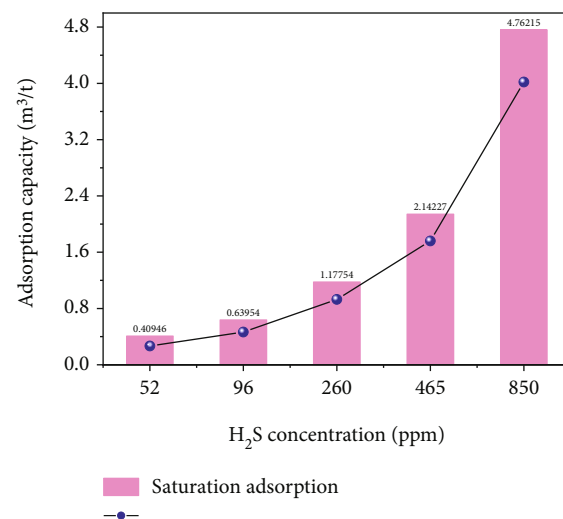


FIGURE 4: Relationship between H₂S concentration and saturation adsorption capacity.

formed at C 1 s (284.6 eV). The Casa XPS software was used to fit the sulfur peaks onto the coal surface.

3. Results and Discussion

3.1. Effect of H₂S Concentration on H₂S Adsorption by Coal.

The changes in temperature, pressure, and H₂S concentration in the adsorption chamber during the adsorption of coal at different concentrations of H₂S are shown in Table S1.1 and Table S1.2 in the Appendix. From the data, the curve for the adsorption amount of H₂S on the dry coal sample over time can be obtained at different concentrations of H₂S, as shown in Figure 3. The relationship between H₂S

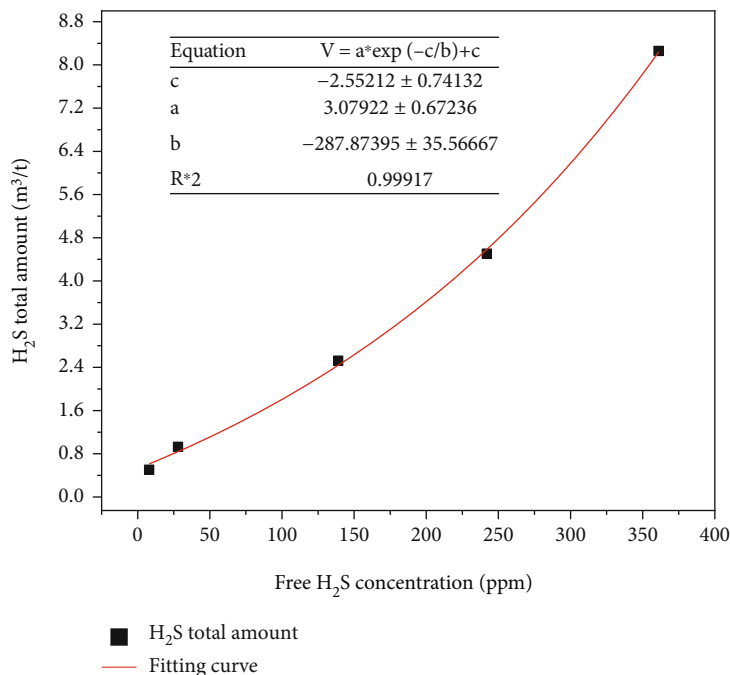


FIGURE 5: Relation curve between free H₂S concentration and total H₂S in dry coal.

concentration and the saturation adsorption amount is shown in Figure 4.

In Figure 3, the rate of adsorption of H₂S on the coal samples at different concentrations of H₂S was the fastest at the beginning of the 2 h; the adsorption rate of H₂S on the coal samples gradually slowed down between 2 h and 20 h; the adsorption generally reached equilibrium between 20 h and 24 h. The average value of the adsorption amount during this period was taken as the saturation adsorption amount of H₂S on the coal samples. Figure 4 shows that the saturation adsorption capacity of the coal sample is the smallest at 52 ppm H₂S concentration, which is 0.40946 m³/t, and the saturation adsorption capacity of the coal sample was the largest at 850 ppm H₂S concentration, which is 4.76215 m³/t. At any adsorption time, the magnitude of coal adsorption for different concentrations of H₂S was ranked as follows: VSP - 850 > VSP - 465 > VSP - 260 > VSP - 96 > VSP - 52, indicating that the adsorption of H₂S gas on the coal samples showed an increasing trend with the increase in H₂S concentration. This is because, according to the adsorption equilibrium theory, the greater the spatial H₂S concentration, the greater the number of H₂S molecules within the pores of the coal, which leads to greater adsorption of H₂S on the coal.

It was found that H₂S has three main occurrence states in coal mines: adsorbed state, water-soluble state, and free state [24], among which the free state H₂S concentration is most easily measured by instruments. In order to simulate the relationship between the total amount of H₂S endowed in the coal seam and the free H₂S concentration at the working face, the free H₂S concentration in the adsorption chamber in the above experiment was plotted against the total amount of H₂S without considering the H₂S content in the

water-soluble state. As shown in Figure 5, the linear correlation of the fitted Equation (4) was good, with an R² of 0.99917.

In Figure 5, the total amount of H₂S is shown to increase exponentially with the increase in free state H₂S concentration at equilibrium. According to Equation (4), the total amount of H₂S in anhydrous coal seams can be inferred by measuring the free state H₂S concentration at the working face.

$$V = 3.07922 \times e^{C/287.87395} - 2.55212, \quad (4)$$

where V is the total amount of H₂S in the coal seam, m³/t; C is the concentration of free state H₂S in the coal seam when the dry coal sample is at adsorption equilibrium, ppm.

3.2. Effect of Water Content on H₂S Adsorption by Coal. In the experiment that investigates the effect of water content on the adsorption of H₂S by coal, the changes in temperature, pressure, and H₂S concentration in the adsorption chamber are shown in Table S2.1 and Table S2.2 in the Appendix. According to the data, the curve for the adsorption of H₂S over time for coal samples having different water contents is as shown in Figure 6, and the relationship between the water content of the coal samples and the saturation adsorption amount is shown in Figure 7.

According to Figure 6, the adsorption rate of H₂S on coal samples having different moisture contents increased gradually over time, and the adsorption rate was the fastest at the beginning of the 2 h period. After that, the adsorption rate of H₂S on the coal samples slowed down gradually and reached an equilibrium at between 20 h and 24 h. In Figure 7, the saturated adsorption of H₂S on the dry coal sample was the smallest at 3.35899 m³/t; the saturated adsorption of H₂S

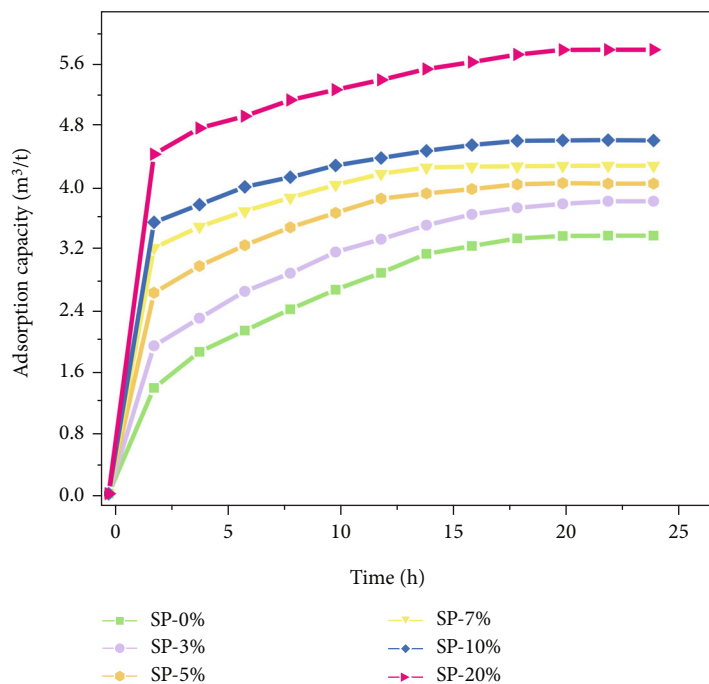


FIGURE 6: Curve of adsorption amount over time for coal samples having different water contents.

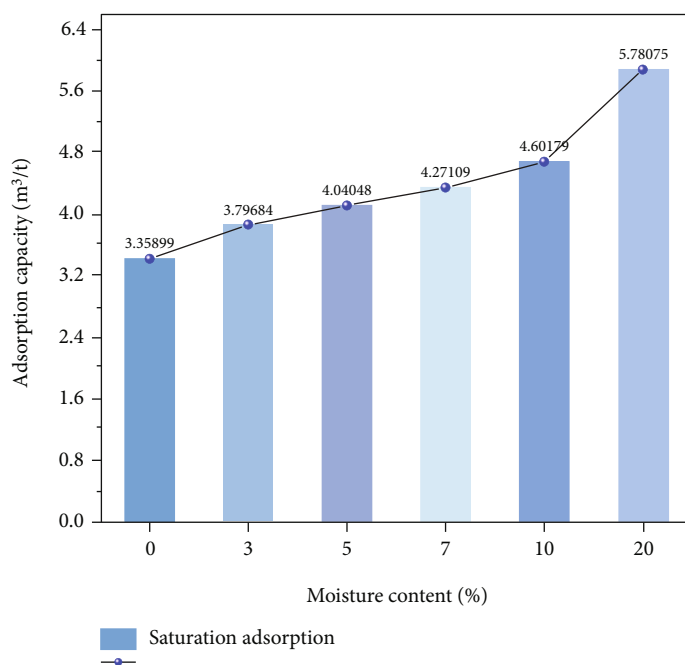


FIGURE 7: Relationship between water content of coal samples and saturation adsorption capacity.

on the coal sample was the largest at 20% water content, which is $5.78075 \text{ m}^3/\text{t}$. The magnitude of H_2S adsorption on coal having different moisture contents over any adsorption time period was ranked as: $\text{VSP} - 20\% > \text{VSP} - 10\% > \text{VSP} - 7\% > \text{VSP} - 5\% > \text{VSP} - 3\% > \text{VSP} - 0\%$, i.e., the adsorption of H_2S on coal increased as the moisture content of the coal samples increased. This is because when the coal sample is dry, H_2S exists in the pores of the coal only in the

adsorbed state. As the water content increases, H_2S is easily soluble in water, and part of H_2S remains in the coal in the water-soluble state, which in turn leads to a decrease in the concentration of H_2S in the space-free state and an increase in the saturated adsorption of H_2S on the coal.

It is known that the occurrence of H_2S in coal seams is related to the water content of the coal. Therefore, to explore the total amount of H_2S in water-bearing coal seams, the

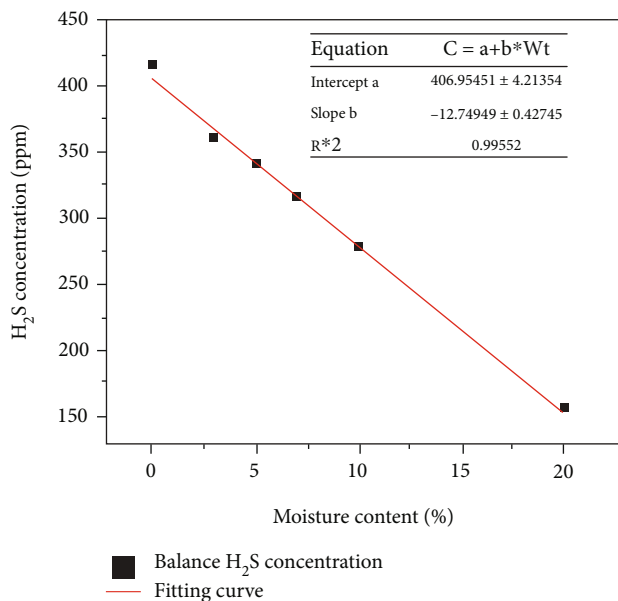


FIGURE 8: Fitting curve of water content and free H₂S concentration.

curve for the water content of the coal samples versus free state H₂S concentration at equilibrium was fitted. As shown in Figure 8, the linear correlation of the fitted Equation (5) was good with R² of 0.99552.

In Figure 8, the concentration of free H₂S at equilibrium decreases linearly with the increase in the water content of the coal sample under the conditions of a certain total H₂S. Therefore, it is presumed that the concentration of free H₂S gas in space can be reduced by injecting water into the coal seam and increasing the water content of the coal seam.

$$C_{H_2S} = -12.74949W_t + C, \tag{5}$$

where C_{H₂S} is the free state H₂S concentration at adsorption equilibrium for aqueous coal, ppm; W_t is the moisture content of the coal sample, %; C is the free state H₂S concentration at adsorption equilibrium for dry coal, ppm.

The equation of the relationship between the total amount of H₂S in the coal seam and the free H₂S concentration and water content of the coal seam can be obtained by associating Equation (4) with Equation (5):

$$V = 3.07922 \times e^{12.74949W_t + C_{H_2S}/287.87395} - 2.55212 \tag{6}$$

where V is the total amount of H₂S in the coal seam, m³/t; W_t is the water content of the coal sample, %; C_{H₂S} is the free state H₂S concentration in the water-bearing coal seam, ppm.

According to Equation (6), the total amount of H₂S in coal seams can be deduced by measuring the water content of coal and the concentration of free state H₂S in space; the total amount of H₂S provides a theoretical basis for H₂S management in coal seams.

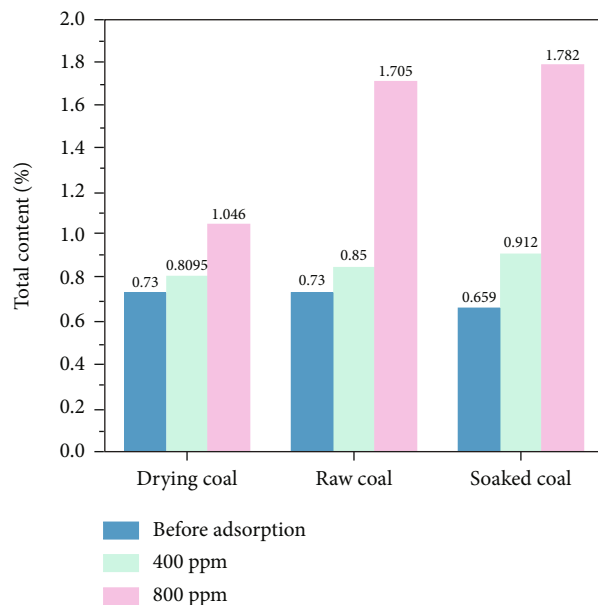


FIGURE 9: Changes of total sulfur content of coal before and after adsorption of H₂S.

3.3. Changes in Sulfur State in Coal before and after H₂S Adsorption. The changes in the total sulfur content of coal before and after the adsorption of H₂S on dry coal samples, raw coal, and water-soaked coal samples are shown in Figure 9. The total sulfur content of all three coal samples increased after adsorption in 400 ppm and 800 ppm H₂S, and the sulfur content increased more significantly after adsorption in 800 ppm H₂S than in 400 ppm, which indicates that the H₂S adsorption process can increase the total sulfur content of coal, and the element S stays in the coal structure in some states after H₂S adsorption. The increase in total sulfur content of the three coal samples after H₂S adsorption was the largest for the water-soaked coal, and the increase in total sulfur content after H₂S adsorption was the smallest for dry coal, indicating that water promotes the conversion of H₂S to sulfur in coal. There are two possible reasons for the increase in the total sulfur content of coal samples after the adsorption of H₂S: one is due to experimental error, where the H₂S molecules that are partially adsorbed into the pores of the coal before the sulfur measurement are not completely removed, which results in an increase in the total sulfur content of the coal; the other is due to the chemisorption of H₂S during the adsorption on coal, where H₂S reacts physically and chemically with active substances in the coal, which results in the elemental sulfur remaining in the structure of the coal.

To investigate the real reason for the increase in the total sulfur content in coal, X-ray photoelectron spectroscopy (XPS) tests were performed on coal samples before and after 800 ppm H₂S adsorption. Organic sulfur in coal is mainly in the form of mercaptans, thioethers, thiophenes, sulfoxides, and sulfones, whereas inorganic sulfur is mainly in the form of sulfide sulfur, sulfate sulfur, and trace amounts of monomeric sulfur [25, 26]. During the XPS test, the 2p layer electrons of sulfur under X-ray excitation undergo energy level

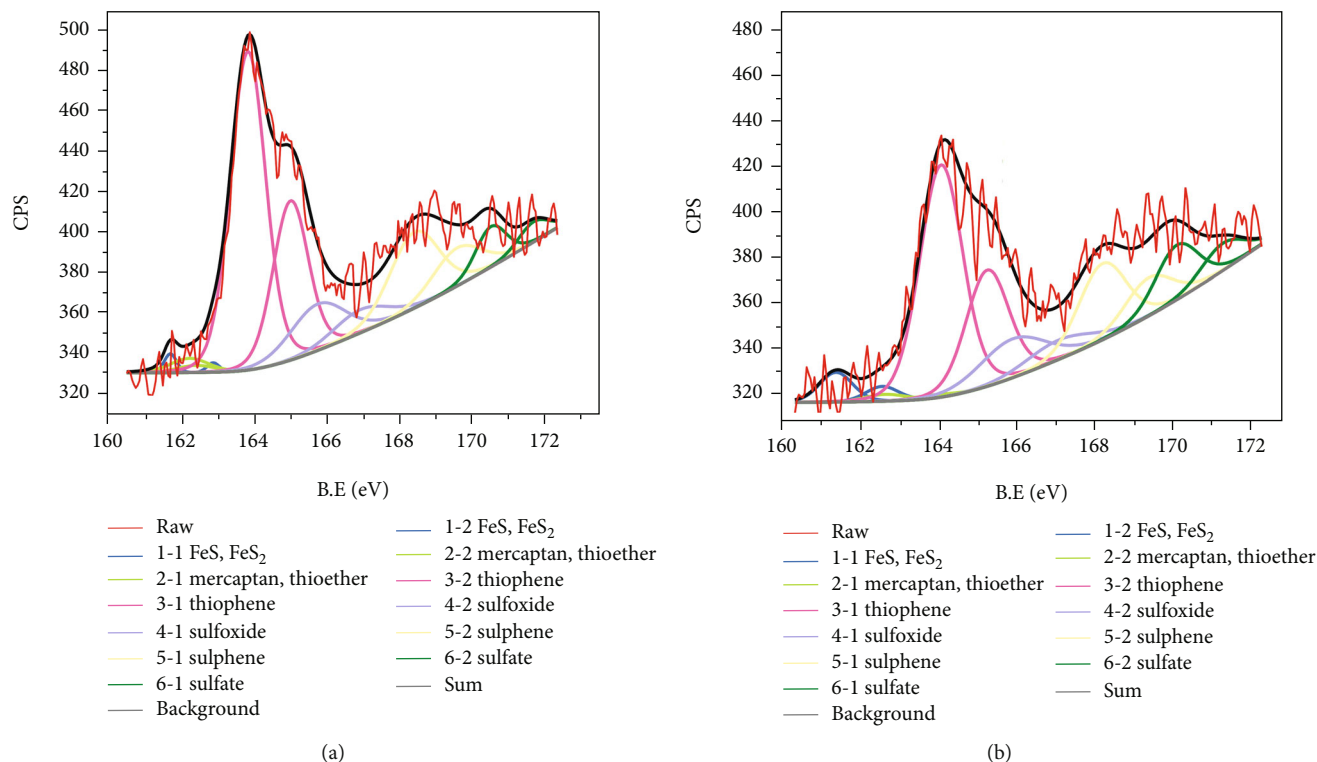


FIGURE 10: XPS spectrum of elemental S before and after H_2S adsorption by SP coal, (a) before adsorption and (b) after adsorption.

TABLE 2: Distribution of sulfur-containing functional groups before and after H_2S adsorption in SP coal.

Coal samples	Functional groups	Peak position (eV)	Content(%)	Coal samples	Functional groups	Peak position (eV)	Content(%)
Before adsorption	FeS, FeS_2	161.91	1.19	After adsorption	FeS, FeS_2	161.40	4.98
	Thiol sulfide	162.44	2.79		Thiol sulfide	162.66	1.33
	Thiophene	164.05	57.45		Thiophene	164.10	50.39
	Sulfoxide	165.98	13.10		Sulfoxide	165.93	13.00
	Sulfone	168.65	19.11		Sulfone	168.23	18.42
	Sulfate, S	170.77	6.36		Sulfate, S	170.13	11.79

splitting, which results in a bimodal form of $2p_{3/2}$ and $2p_{1/2}$ in the XPS spectra. A bimodal spacing of 1.18 eV, a peak area ratio of about 2 : 1, and the same half-peak width [27] were used to fit the XPS spectra of elemental sulfur in coal by this method. The range of binding energies of different sulfur-containing groups are as follows: (160.7–162.3 eV) for FeS, FeS_2 ; (162–163.0 eV) for thiols and thioethers; (163.9–164.9 eV) for thiophenes; (165.0–166.0 eV) for sulfoxides; (167.7–169.3 eV) for sulfones; (169.2–170.8 eV) for sulfates, and monomeric sulfur. The XPS split-peak fitted sulfur spectrum of SP coal is shown in Figure 10, with 6 binding energies and 12 characteristic peaks. The types and content of each sulfur-containing functional group are shown in Table 2.

According to the XPS fitting results, the organic sulfur in SP raw coal is mainly thiol, thioether, thiophene, sulfoxide, and sulfone, and the inorganic sulfur is mainly FeS, FeS_2 , sulfate, and monomeric sulfur. The proportion of thiophene is the highest, at 57.45%, indicating that thiophene is the

main form of sulfur in SP coal, whereas the proportion of FeS and FeS_2 is the lowest, at 1.19%. The content column shows that the percentage content of organic sulfur, such as mercaptan, thioether, thiophene, sulfoxide, and sulfone in the coal samples exhibits a decreasing trend after the adsorption of H_2S gas, whereas the percentage content of inorganic sulfur, such as FeS, FeS_2 , sulfate, and monomeric sulfur, shows an increasing trend. This may be because the increase in the organic sulfur content of coal is small or unchanged after H_2S adsorption, whereas the increase of inorganic sulfur content is significant, which leads to a decrease in the proportion of organic sulfur content. This suggests that the increase in the total sulfur content of coal during H_2S adsorption is mainly due to the conversion of H_2S to the inorganic sulfur component of coal.

3.4. Occurrence Relationship of Sulfur and H_2S in Coal. From the above experiments, the adsorption of H_2S on coal is a chemical adsorption process in addition to a physical

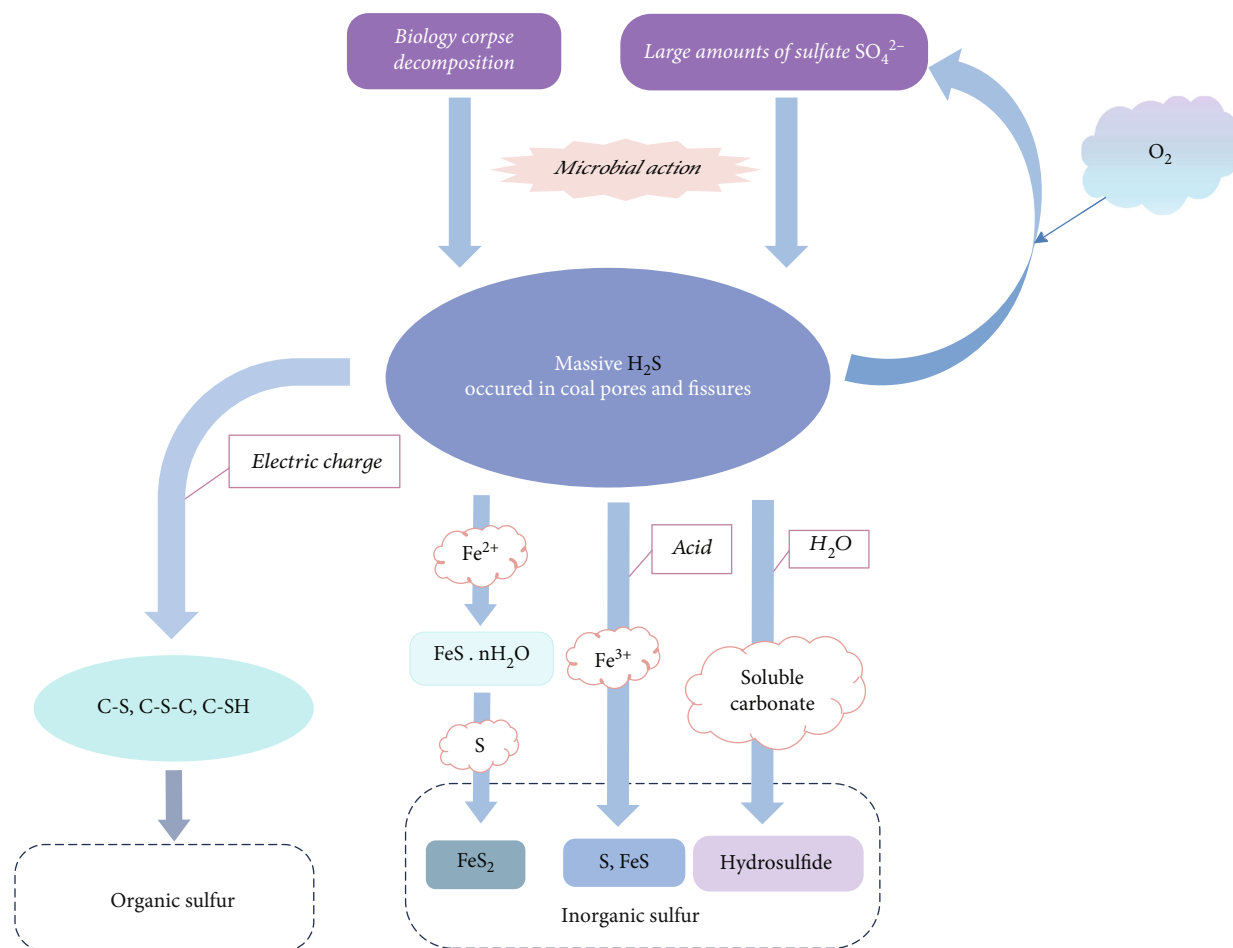
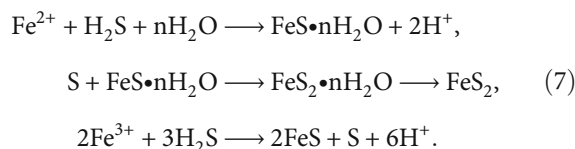


FIGURE 11: Occurrence relationship between sulfur and H₂S in coal.

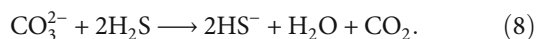
adsorption process, which is mainly reflected in the increase of total sulfur content in the coal, with the most obvious increase of inorganic sulfur content. Because the mechanism of H₂S adsorption on coal is still inconclusive, and the properties and structures of activated carbon are similar to coal, the mechanism of H₂S adsorption on coal can be inferred from the research results of H₂S adsorption on activated carbon. Deng et al. [28] found that there is both physical and chemical adsorption of H₂S on activated carbon, and when chemisorption occurs, H₂S combines with an aromatic carbon in activated carbon under the action of electric charge to form structures such as thiophene, C-S-C, and C-SH. Based on this, the occurrence relationship between sulfur and H₂S in coal is presumed to be as shown in Figure 11.

H₂S gas endowed in coal pores and fissures has two main sources. A small part is from the decomposition of dead plants and animals, and most comes from the reduction of SO₄²⁻ [6], where in poorly sealed coal seams, H₂S can be oxidized again by O₂ to SO₄²⁻. Similar to activated carbon, coal contains a large number of aromatic carbon functional groups, and it is speculated that after coal adsorption of H₂S, H₂S combines with these functional groups and remains in the coal structure in the form of organic sulfur such as thiophene, C-S-C, and C-SH, which in turn leads to an increase in the total sulfur content of the coal.

On the other hand, during the coal-forming stage, a large number of Fe ions are carried out of the deposited strata in the form of Fe(OH)₃ colloidal solution and remain in the coal seam as stable complexes. Some Fe³⁺ are reduced to Fe²⁺ within the coal seam, and Fe²⁺ can react with H₂S to form hydrometallic iron sulfide (FeS·nH₂O), which reacts with sulfur monomers and transforms into pyrite after crystallization and dehydration; [29, 30] while the other Fe³⁺ can react directly with H₂S under acidic conditions to form ferrous sulfide and S monomers according to the following reaction equation.



In addition, it is known from the composition of coal [31] that coal contains a large amount of carbonate components, and with the participation of water, some soluble carbonates can react with H₂S, which results in a portion of H₂S remaining in the coal in the form of sulfur hydrides. The reaction equation is as follows:



Because the reaction process of H_2S converting to inorganic sulfur is ionic, water promotes the conversion of H_2S to inorganic sulfur in coal, which is consistent with the experimental result that water-soaked coal has the largest increase, of the three coal samples in Figure 9, in total sulfur content after the adsorption of H_2S . In Figure 9, the total sulfur content of dry coal also increases after adsorption of H_2S . Therefore, it can be inferred that after adsorption of H_2S , a small portion of H_2S is converted to organic sulfur forms such as thiophene, C-S-C, and C-SH, and most H_2S is converted into inorganic sulfur forms such as sulfur hydride, iron sulfide sulfur, and monomeric sulfur with the participation of water, which in turn leads to an increase in the total sulfur content of coal. Therefore, during the process of H_2S adsorption by coal, both physical and chemical adsorption processes occur, and there is a positive correlation between the total sulfur content of coal and the occurrence of H_2S in coal seams, i.e., the higher the total sulfur content in coal, the greater the occurrence of H_2S in coal seams.

4. Conclusions

- (1) At the atmosphere temperature and pressure, the adsorption of H_2S by coal generally reaches equilibrium at 24 h. The adsorption of H_2S increases with the increase in spatial H_2S concentration and the water content of the coal samples. In addition to physical adsorption, the chemical adsorption of H_2S on coal also occurs. The total sulfur content of coal increases after adsorption of H_2S , and water promotes the conversion process of H_2S to sulfur in coal
- (2) SP raw coal has the highest proportion of thiophene sulfur and the lowest proportion of FeS and FeS_2 . The inorganic sulfur content increases significantly after adsorption of H_2S , and most of the H_2S remains in the coal structure in the form of inorganic sulfur, such as sulfur hydride, iron sulfide sulfur, and monomeric sulfur, and a small proportion of H_2S is bonded in the structure of the coal in the form of organic sulfur such as thiophene, C-S-C, and C-SH. Therefore, the higher the total sulfur content in coal, the greater the occurrence of H_2S
- (3) The total amount of H_2S increases exponentially with the concentration of free H_2S at equilibrium and the water content of the coal. The total amount of H_2S in the coal seam can be inferred by measuring the concentration of free H_2S in space and the water content of the coal seam according to the fitting equation. Under the condition that the total amount of H_2S is certain, the concentration of free H_2S decreases linearly with the increase in the water content of the coal sample. It is therefore inferred that the concentration of H_2S in space can be reduced by injecting water into the coal seam, which provid-

ing a theoretical basis for the management of H_2S in underground coal mines

Data Availability

The (H_2S concentration) data used to support the findings of this study are included within the supplementary information files. The remaining data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

GAO Fei is responsible for conceptualization, methodology, and investigation. JIA Zhe is responsible for the supervision and editing. XIA Ji is responsible for data curation, writing, and original draft preparation. WANG Dapeng and YANG Yulong are responsible for project administration. SHAN Yafei is responsible for the methodology. SHEN Jiaqi is responsible for validation and editing.

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Supplementary Materials

the Supplementary Files provided in this paper are mainly the data summary of Section 3.1 and 3.2. (*Supplementary Materials*)

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