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Research Article

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The Effect of Water-based Slurry Addition on the Surface Functional Groups of Gas-bearing Coal

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Abstract: The effect of water-based slurry treatment on the surface functional groups of low-rank coal plays a crucial role in the study of gas adsorption and desorption in gas-bearing coal. This study shows that the water-based slurry significantly enhances the hydrophilicity of the coal surface by introducing polar functional groups (such as thiol, phenolic sulfur, C=O, and sulfone) and reducing hydrophobic functional groups (such as C-C and C-H). This change leads to the formation of a water film on the coal surface, which effectively inhibits the adsorption and desorption of gas. Specifically, the increase in polar functional groups enhances the chemical stability and hydrophilicity of the coal, further weakening the coal's ability to adsorb gas molecules and reducing the gas desorption rate. Moreover, the increase in pyrrole-type nitrogen and the decrease in nitrogen oxides suggest structural changes on the coal surface, further suppressing the diffusion and desorption of gas. Therefore, water-based slurry treatment provides an effective method to reduce gas adsorption and desorption, contributing to the safe exploitation of low-rank coal.

Keywords: Water-based slurry; low-rank coal; surface functional groups of coal; gas adsorption and desorption

1. Introduction

Coal resources still play a dominant role in China's energy structure [1], and the associated gas, as a high-efficiency clean energy, has garnered widespread attention in recent years [2]. According to reports, China's coal seam gas reserves rank third in the world, behind only Russia and Canada, and are considered an important alternative resource in the energy revolution [3-4]. However, during the extraction process, the gas present in the coal is a highly hazardous disaster gas, which can cause various safety accidents during mining operations, whether in high-gas or low-gas mines [5]. For the sustainable and safe production of coal mines, preventing and controlling coal mine gas accidents is urgent. Currently, the mainstream method for gas control is a comprehensive approach that strengthens ventilation and implements gas drainage pipelines. Additionally, extensive practice has shown that coal seam water injection (water) is an effective measure for gas control in working faces [6]. Injecting water into the coal seam or spraying water on the coal face not only wets the coal but also improves the gas desorption characteristics. The moisture retained in the coal's micropores helps reduce gas desorption volume and desorption rate, playing an inhibitory role. Furthermore, Xu Yanpeng et al. [7] proposed a method using water-based slurry to rapidly wet the coal, suppress gas disruption, eliminate outburst risks, and reduce underground gas concentrations. Water-based slurry is more effective than pure water in suppressing gas desorption, and it has broad application prospects, especially in preventing gas outbursts and avoiding gas exceeding safety limits, which deserves further research. The essence of coal's gas adsorption and desorption is the interaction between methane molecules and coal macromolecules [8]. Scholars at home and abroad have found that coal's gas adsorption is not only influenced by pore structure but also closely related to the coal's surface functional groups [9]. HAO et al. [10] used a combination of scanning electron microscopy and X-ray photoelectron spectroscopy to study the effect of oxygen-containing functional groups in coal on gas adsorption. They found that the more oxygen-containing functional groups on the coal surface, the stronger the hydrophilicity of the coal, which is unfavorable for gas adsorption. Zhang Jin et al. [11] studied the role and mechanism of surface functional groups in coal's gas adsorption and found that the presence of nitrogen functional groups affects coal's gas adsorption performance. Overall, nitrogen-containing functional groups enhance the coal's methane adsorption capacity. Xi Jianhua et al. [11] used molecular simulations to show that nitrogen functional groups in coal, such as pyridine nitrogen, promote adsorption, while pyrrole nitrogen hinders adsorption. Based on this, the present study uses X-ray photoelectron spectroscopy (XPS) to analyze the changes in coal surface functional groups under the effect of water-based slurry and their impact on gas adsorption and desorption.

2.Materials and Methods

Water-based Slurry and Test Samples

The water-based slurry is a colorless and transparent gel-like aqueous solution formed by dissolving a wetting agent and a thickener in water in a certain proportion. It has stable characteristics such as gelation, film formation, adhesion, masking, and controlled release, along with strong hydrophilicity and water retention properties. The prepared water-based slurry is shown in Figure 1(a). A large beaker is used, and coal samples with a particle size smaller than 200 mesh are first added. The water-based slurry is then poured in, and the coal sample is thoroughly stirred to ensure complete immersion (the immersion state is shown in Figure 1(b)). After one week of immersion, the coal sample is subjected to low-temperature drying. Once dried, the sample is sealed and stored, with labels applied according to the degree of coal maturation for subsequent experiments.

(a) Water-based slurry *(b) Test coal sample*

Figure 1: Water-based mucilage and soaked coal samples

Coal Sample Preparation and Analysis

The experiment selected fresh low-rank coal samples from the Changyan coal seam in the Shendong mining area. After collecting the coal samples, they were placed in sealed bags and brought back to the laboratory. Fresh, uncontaminated coal samples from the interior of the coal body were selected for grinding and sieving. Standard sieves were then used to select two different particle sizes: 60-80 mesh and below 200 mesh. The samples were placed in sealed bags and labeled according to their degree of metamorphism and particle size for future use in experiments. The coal samples with a particle size of 60-80 mesh were placed in a 105°C vacuum drying oven and dried for 8 hours. After drying, they were stored in sealed bottles for industrial and elemental analysis. The test results are shown in Table 1.

Table 1: Industrial and elemental analyses

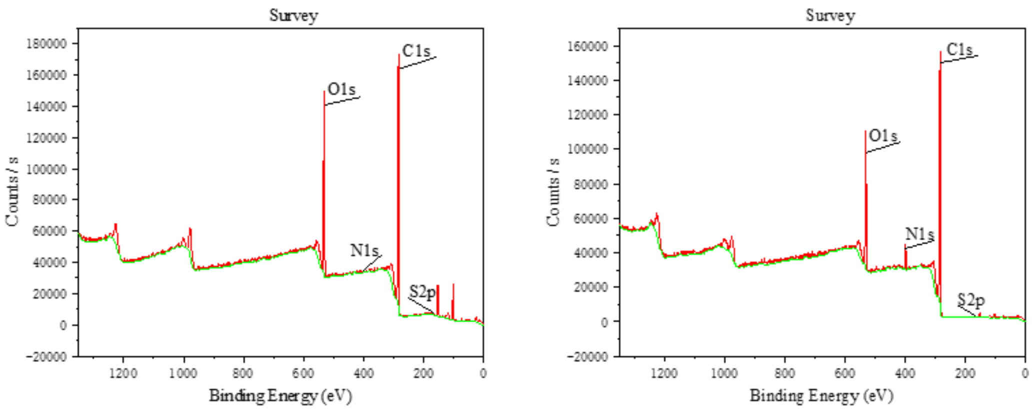
Coal rank	Industrial analysis /%				Total sulfur	Elemental analysis /%			
	M_{ad}	A_{ad}	V_{daf}	FC_d	$S_{t.d}$	O	C	H	N
Low-rank coal	4.17	8.72	35.63	51.48	0.31	15.54	78.53	4.76	0.86

Testing Instruments

X-ray photoelectron spectroscopy (XPS) was used for testing, with the Thermo Scientific ESCALAB 250Xi instrument. The excitation source is a monochromatic Al target (E = 1486.68 eV), operating at a voltage of 12 kV and a power of 150 W. The vacuum pressure is maintained at P < 10^-8 mBar. The test energy range is 100 eV (survey spectrum) and 30 eV (high-resolution spectrum). The step size for the survey spectrum is 1 eV, and for the high-resolution spectrum, it is 0.05 eV. The testing dwell time is 40-60 ms. Charge correction was performed using the binding energy of C1s = 284.80 eV as the reference, and the results for the carbon spectrum, S2p, O1s, N1s, and C1s high-resolution and survey spectra were obtained in data form.

3.Results and Discussion

The XPS spectrum test results for low-rank coal treated with water-based slurry are shown in Figure 2. This spectrum allows for qualitative analysis of the coal's structure and provides information about the functional groups present. To characterize the structure further, a quantitative analysis of the content of each functional group is necessary. Therefore, peak fitting of the XPS spectrum was performed to determine the content and positions of the functional groups, with the fitted peaks shown in Figures 3 and 4. The PeakFit software was used to perform peak fitting on the NMR data, adding as many peak positions as possible to ensure a higher degree of fitting and accuracy, so that the peak fitting results more closely align with the experimental data. The assignment of each peak structure is based on the binding energy values, and the relative area of each sub-peak is used to represent the content ratio of the functional groups. The peak binding energy assignments and contents for low-rank coal in the XPS spectrum are shown in Table 2.



(a) Low-rank raw coal *(b) Low-rank coal treated with water-based slurry*

Figure 2: Full spectrum of low-rank coal

From Table 2, it can be seen that after treatment with water-based slurry, the sulfur content in low-rank coal (XPS S2p) shows the following changes: the content of thiol phenolic sulfur increases (3.94% → 18.73%), which is a polar functional group. Its increase likely enhances the coal's affinity with water molecules, forming a water film that covers the coal surface. This hydrophilic shielding effect reduces the coal's ability to adsorb gas and also limits the gas desorption process. This indicates that the water-based slurry introduces a hydrophilic structure, which exerts a dual inhibitory effect on gas adsorption and desorption. The content of thiophene sulfur increases (15.35% → 19.24%), and since thiophene sulfur is a stable aromatic structure, it has limited influence on the physical adsorption and desorption of gas. The slight increase in its content may be related to changes in the chemical composition of the coal surface, but its effect on gas suppression is weak. The content of sulfone sulfur decreases (24.00% → 4.71%), and as sulfone is a highly polar group, its reduction might lower the coal's hydrophilicity. However, because water-based slurry treatment introduces more thiol phenolic sulfur, the overall hydrophilicity still increases. Therefore, the reduction of sulfone sulfur does not significantly weaken the inhibition of gas adsorption. The content of sulfoxide sulfur increases (5.75% → 7.85%), and sulfoxide sulfur, being a moderately polar oxidation sulfur structure, contributes to the enhancement of coal's hydrophilicity, further inhibiting gas adsorption and hindering the desorption process. The inorganic sulfur content remains nearly unchanged (50.96% → 49.47%), and inorganic sulfur, being chemically stable, has little impact on the suppression of gas adsorption and desorption after the water-based slurry treatment.

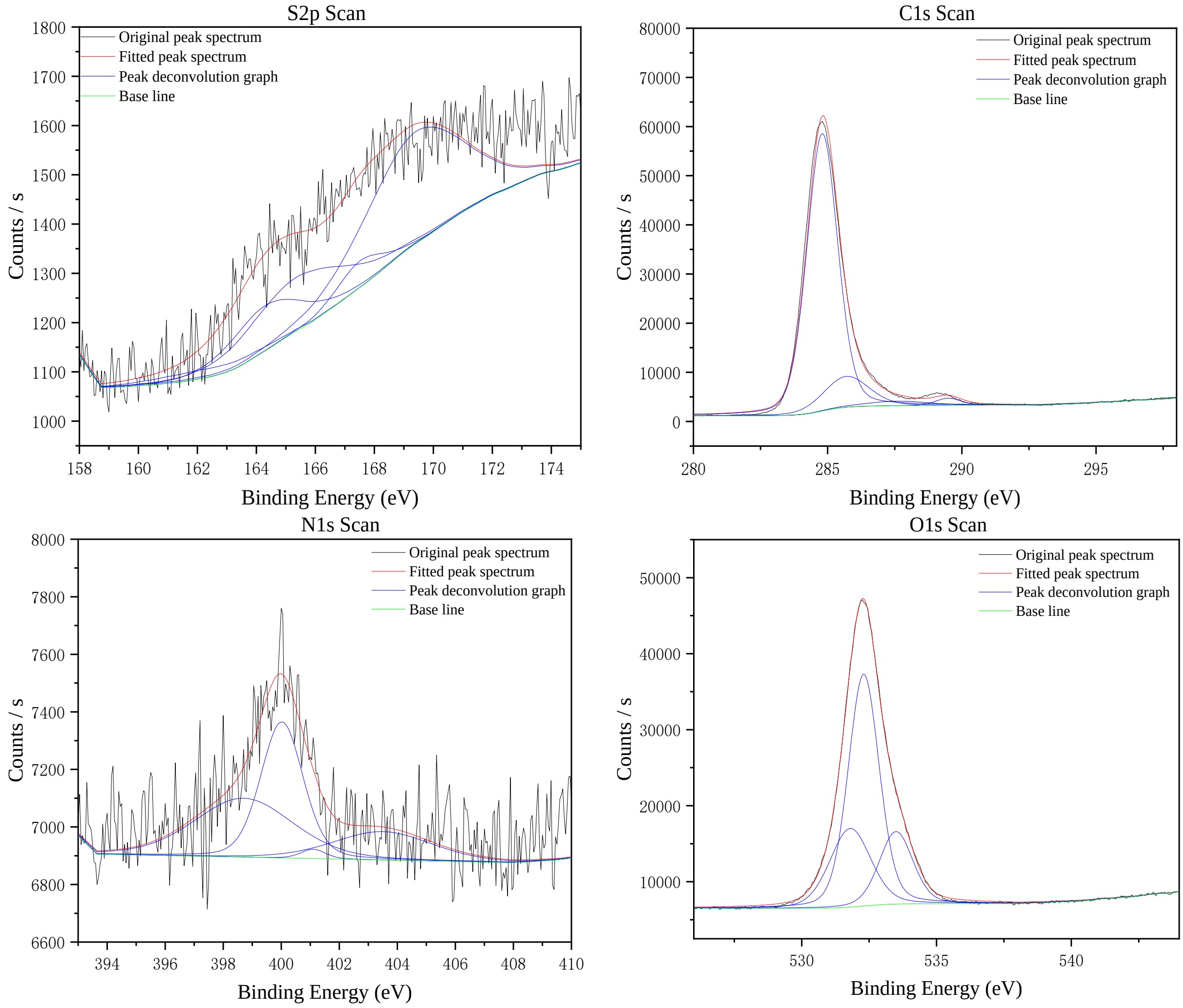
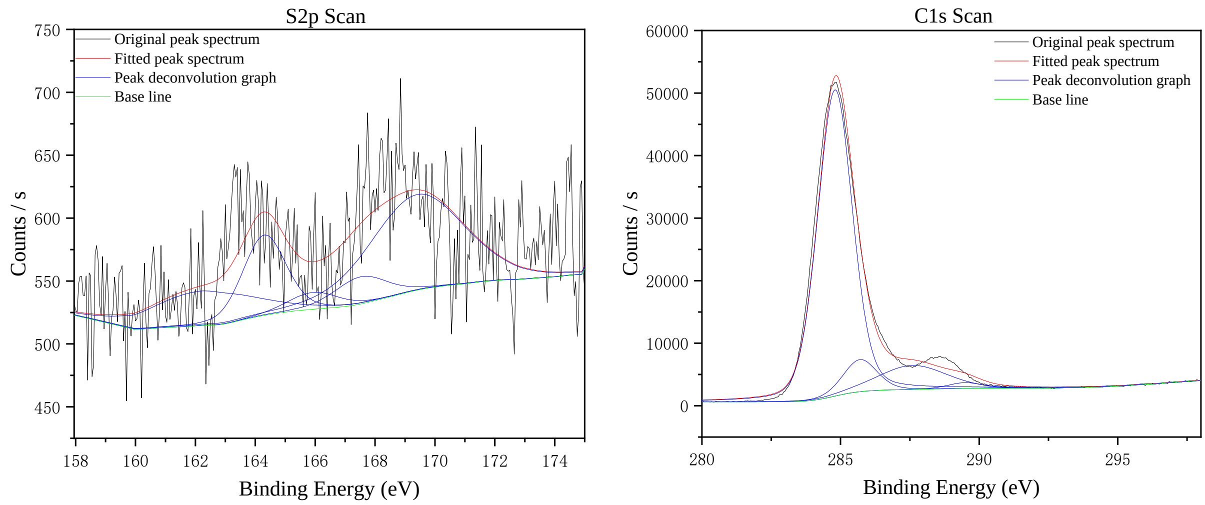


Figure 3: XPS peak fitting spectrum of low-rank raw coal



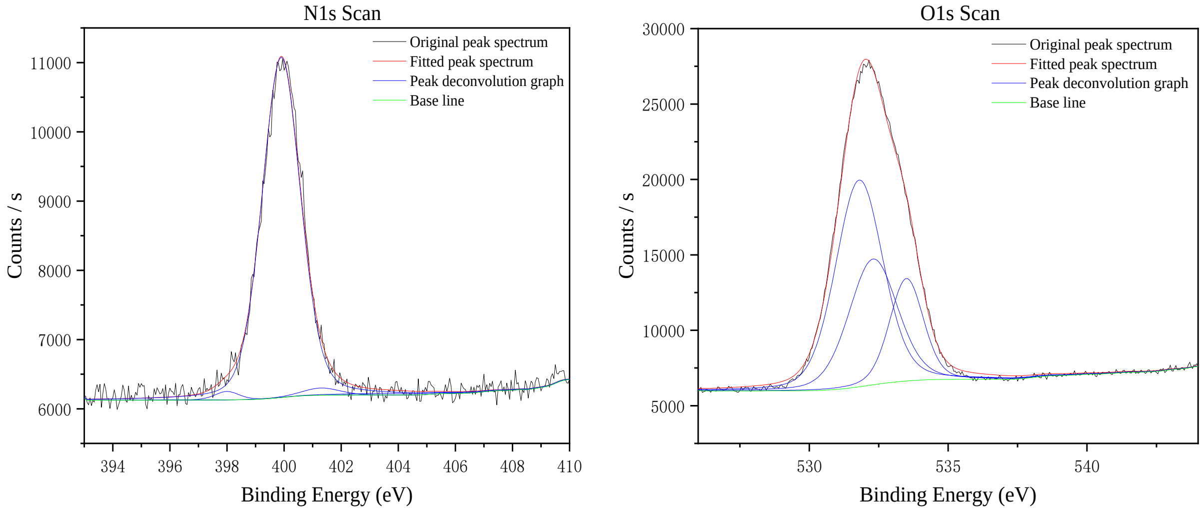


Figure 4: XPS peak fitting spectrum of low-rank coal after water-based slurry treatment

Table 2: The peak assignments corresponding to the binding energy of low-rank coal

Project	**Low-rank raw coal**			**Low-rank coal treated with water-based slurry**		
	Binding energy (eV)	**Peak assignment**	**Proportion%**	**Binding energy (eV)**	**Peak assignment**	**Proportion%**
XPS S2p	162.23	Thiolphenolic sulfur	3.94	162.23	Thiolphenolic sulfur	18.73
	164.30	Thiophene sulfur	15.35	164.30	Thiophene sulfur	19.24
	165.37	Sulfone sulfur	24.00	165.93	Sulfone sulfur	4.71
	167.52	Sulfoxide sulfur	5.75	167.52	Sulfoxide sulfur	7.85
	169.40	Inorganic sulfur	50.96	169.40	Inorganic sulfur	49.47
XPS C1s	284.80	C-C, C-H	82.16	284.80	C-C, C-H	78.57
	285.70	C-O	13.33	285.70	C-O	8.01
	287.60	C=O	2.73	287.60	C=O	11.94
	289.50	OH	1.78	289.50	OH	1.48
XPS N1s	398.70	Pyridine nitrogen	39.29	398.00	Pyridine nitrogen	1.50
	400.02	Pyrrole nitrogen	40.14	399.90	Pyrrole nitrogen	95.39
	401.10	Quaternary nitrogen	1.60	401.30	Quaternary nitrogen	1.95
	403.50	Nitrogen oxides	18.97	403.70	Nitrogen oxides	1.16
XPS O1s	531.80	C=O	24.89	531.80	C=O	50.54
	532.30	C-O	56.11	532.30	C-O	31.46
	533.50	COO-	19.00	533.50	COO-	18.00

In the carbon element (XPS C1s), the contents of C-C and C-H decrease (82.16% → 78.57%), indicating a reduction in hydrophobic groups and an increase in hydrophilicity. Since the water-based slurry mainly introduces polar structures, the coal surface may be covered by water molecules, obstructing the adsorption and diffusion of gas molecules. This decrease in hydrophobicity helps to suppress gas adsorption. The content of C-O decreases (13.33% → 8.01%), which would typically weaken the coal's hydrophilicity. However, due to the increase in thiol phenolic sulfur and C=O groups, the overall hydrophilicity of the coal still increases. This decrease may result from chemical reactions that remove weaker polar groups while stronger polar groups are introduced. The content of C=O increases (2.73% → 11.94%), and the significant increase in C=O groups enhances the coal's polarity and hydrophilicity, which shields gas adsorption through a water film. Additionally, the increase in C=O groups may create strong adsorption sites on the coal surface, stabilizing the water molecule layer and further reducing the gas desorption efficiency. The content of OH functional groups decreases (1.78% → 1.48%), indicating the removal of some weaker polar structures, but this does not significantly affect the overall polarity and hydrophilicity of the coal. The reduction of OH groups does not weaken the inhibitory effect of the water-based slurry treatment.

In the nitrogen element (XPS N1s), the content of pyrrole-type nitrogen increases dramatically (40.14% → 95.39%). Pyrrole-type nitrogen, being a non-polar aromatic structure, has strong stability. Its significant increase likely enhances the coal's surface structural density, further restricting the diffusion paths of gas molecules, thereby suppressing gas adsorption and desorption. The content of pyridine-type nitrogen decreases (39.29% → 1.50%), and since pyridine-type nitrogen is a polar group, its decrease may reduce the coal's polarity. However, the increase in thiol phenolic sulfur and C=O compensates for this reduction, and the overall hydrophilicity of the coal does not decrease significantly. The reduction of pyridine-type nitrogen may also be related to the reconstruction of surface functional groups, further enhancing the inhibition of gas adsorption. The content of nitrogen oxides decreases (18.97% → 1.16%), and since nitrogen oxides are strongly polar groups, their reduction lowers the coal surface's polarity and adsorption active sites. However, due to the increase in other polar groups (such as C=O), the suppression of gas adsorption on the coal surface still increases.

In the oxygen element (XPS O1s), the content of C=O increases significantly (24.89% → 50.54%), indicating enhanced coal surface polarity and an improved ability to adsorb water molecules. This change leads to the formation of a water film on the coal surface, which significantly inhibits gas adsorption and reduces the gas desorption rate. The content of C-O decreases (56.11% → 31.46%), but this reduction does not significantly weaken the coal's polarity. Combined with the increase in C=O, the coal's ability to absorb water still significantly increases. This change mainly reflects the chemical modification effect of the water-based slurry treatment. The content of COO- decreases slightly (19.00% → 18.00%), and although this has a small effect on the coal's polarity, it may indicate that some weaker polar groups have been removed by the water-based slurry treatment. This change does not significantly affect the inhibition of gas adsorption and desorption.

4. Conclusion

1. The water-based slurry significantly enhances the hydrophilicity of low-rank coal surfaces by introducing polar functional groups (such as thiol phenolic sulfur, C=O, and sulfone sulfur) and reducing non-polar hydrophobic groups (such as C-C and C-H). This makes the coal surface more prone to adsorb water molecules, forming a water film that shields the surface, thus inhibiting the coal's ability to adsorb gas.
2. The increase in polar functional groups (such as C=O and thiol phenolic sulfur) and a significant rise in pyrrole-type nitrogen content enhance the chemical modification effect on the coal surface, further restricting the diffusion and desorption pathways of gas molecules, effectively reducing the gas desorption rate.
3. The water-based slurry treatment inhibits both gas adsorption and desorption by reducing surface hydrophobicity and forming a chemical shielding layer. This provides an effective technological solution for the safe mining and utilization of low-rank coal with high gas content.

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