Experimental Study on the Pore Structure and Maceral Components of Low-Rank Coal Treated with Mixed Acid Solutions

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Abstract: To achieve the optimal acidification and permeability enhancement effect for low-rank coal, this study focuses on the coking coal from the Camel Mountain mine. The results indicate that the orthogonal design and dissolution rate experiments found that the best dissolution effect is achieved when the acid mixture is composed of a mass fraction of 6% HCl solution plus a mass fraction of 9% HF solution, reacting at 35°C for 6 hours. This level has been verified to have an average dissolution rate of 4.65%. After acidification, the pore structure evolves from complex ink bottle-shaped pores to open parallel plate pores. The main clay components, calcite and dolomite, in the coal sample experience a sharp decrease and disappearance in diffraction intensity after acidification. Industrial analysis shows that the a and b values decrease by 1.103 times and 1.31 times, respectively, after acidification. The ash content is reduced from 29.3% to 20.1%, and the fixed carbon increases from 67.34% to 73.44%.

***Keywords*:** low-rank coal, dissolution rate experiment, low-temperature nitrogen adsorption, XRD diffraction

1. Introduction

Gas extraction is a key strategy for reducing the risk of gas explosions and is an effective way to achieve the efficient use of gas resources. With the continuous increase in mining depth, many coal seams in China face problems such as high gas pressure, loose coal texture, and insufficient permeability. Traditional gas extraction technologies are inefficient and cannot meet current mining demands. [1] Academic research both domestically and internationally has indicated that there is a widespread deposition of large amounts of carbonate and clay minerals in the pores and fractures of coal seams. These deposits reduce the volume of pores and the porosity, and decrease the connectivity between pores, thereby reducing the permeability of the coal seams.[2][3]This condition severely hinders the flow of gas within the coal seams, posing a significant obstacle to improving the efficiency of gas extraction [4]. Cheng Xiaoqian[5] conducted acidification experiments on coal seams in low-rank coal mine areas of Xinjiang. The acidification process can cause carbonate rock minerals to react with the acid solution, dissolving the carbonate minerals that fill the pores, which leads to an increase in pore volume and has a positive effect. Ni Xiaoming [6] and others' research results indicate that acidic substances with multiple components can interact with the mineral components in coal seams, a process that helps to enhance the permeability of the coalbed storage area.

The article conducts a specific analysis of the mineral composition of the coal seam at the Camel Mountain Mine. It determines the optimal ratio of acid solution based on the orthogonal dissolution rate experiment of coal powder, and characterizes the changes in the pore structure of the coal samples through isothermal nitrogen adsorption experiments. The impact of the acid solution on the mineral components of the coal samples is determined by industrial analysis and XRD diffraction technology, with the expectation that the acidification technology will provide some theoretical reference for the acidification and permeability enhancement of low-permeability coal seams at the Camel Mountain Mine.

2. Characteristics of Coal Reservoirs and Experimental Samples

The coal samples used in the experiment were collected from the Luotuoshan Mine of Wuhai Energy Co., Ltd., with a vitrinite reflectance of 0.45%, classifying it as low-rank coal. Fresh coal samples collected from underground were analyzed for mineral composition and industrial analysis using an X-ray diffractometer. See Tables 1 and 2.

Table 1. Mineral matter content fraction in coal

Sample	Mineral matter mass fraction(%)	The relative mass fractions of various minerals in coal (%)				
		Calcite	Dolomite	Kaolinite	Quartz	Illite/Montmorillonite mixed layers
Luotuoshan	38.44	49.57	38.22	9.12	2.57	0.52

Table 2. Industrial Analysis

a(ml/g·r)	b(MPa^{-1})	Aad(%)	Mad(%)	Vad(%)	True density(t/m^3)	Apparent density(t/m^3)	Pore volume.(m^3/m^3)
23.597	0.483	29.3	0.43	25.26	1.61	.1.48	0.055

As can be seen from Table 1, the mineral content in the low-rank coal samples from the Luotaoshan Mine is relatively high, with the carbonate mineral components of calcite and dolomite accounting for 87.79%, while the remaining silicate clay materials account for only 12.21%. From Table 2, it is known that the ash content of the Luotaoshan low-rank coal is high, which may indicate a significant amount of clay fillings.

3. Experimental Methods and Results Analysis

3.1 Orthogonal Dissolution Rate Experiment with Acid Mixture Proportions

By calculating the dissolution rates under different orthogonal designs, the following results of the orthogonal experimental scheme are obtained in Table 3, and the variance analysis of the dissolution rates is presented in Table 3.

Table 3. Industrial Analysis

Number	Influencing factors				Criterion
	HCL(%)	HF(%)	time(h)	temperture(°C)	Dissolution rate.(%)
1	6	3	6	25	3.21
2	6	6	24	30	4.51
3	6	9	12	35	4.41
4	9	3	24	35	2.92
5	9	6	12	25	2.94
6	9	9	6	30	4.14
7	12	3	12	30	3.4
8	12	6	6	35	4.5
9	12	9	24	25	3.5
K1	12.13	9.53	11.85	9.65	
K2	10	11.95	10.75	12.05	
K3	11.4	12.05	10.93	12.05	
k1	4.043	3.1767	3.95	4.0167	
k2	3.333	3.9833	3.5383	4.0234	
k3	3.8	4.0167	3.6433	4.0344	
R	0.71	0.84	0.37	0.8067	
Optimal combination: A_1,B_3,C_1,D_3					

As can be seen from Table 4, the order of factors affecting the acidification effect from the most to the least significant is B, D, A, C, indicating that the mass fraction of HF has the greatest impact on the experiment, while temperature has the least impact on the experimental indicator. Based on the ki, the optimal parameter combination for acidification effect is A1B3C1D3, which means that the acidification effect is the best when the mass fraction of HCl is 6%, the mass fraction of HF is 9%, the reaction time is 6 hours, and the temperature is 35°C.

3.2 Isothermal Nitrogen Adsorption Experiment

When conducting pore structure analysis using the low-temperature liquid nitrogen adsorption method, the commonly used BBH (Brunauer-Bodart-Holmes) pore classification method is applied.

From Figure 1, it can be seen that the N2 adsorption mechanism is reversible physical adsorption through van der Waals forces, and during the adsorption process, there is a transition from monolayer adsorption to multilayer adsorption. In English, The adsorption/desorption curve of coal before acidification utilizes nitrogen gas during the condensation and evaporation process, which generates different relative pressures, forming corresponding hysteresis loops that reflect the morphology of pore development. The adsorption and desorption curves in Area A are closely aligned, showing characteristics of monolayer adsorption, indicating excellent reversibility. This characteristic is typically associated with microporous structures of smaller diameters. Area B corresponds to the initial multilayer adsorption, where the adsorption curve gradually separates, but the difference is not significant, indicating that there are still some blind pores in the pores corresponding to this area. Area C corresponds to capillary condensation, with a clear hysteresis loop appearing, and its desorption curve has a section of a saturated adsorption platform, indicating that the pore structure of the original coal sample from Camel Mountain is complex, suggesting the presence of ‘ink bottle pores’. However, after acidification, the capillary phenomenon disappears, indicating that the ‘ink bottle pores’ develop into open parallel plate pores under the etching action of acidification, simplifying the complex pore structure. The N_2 adsorption-desorption amount after acidification is significantly lower than that before acidification, reflecting the simplification of the pore structure.

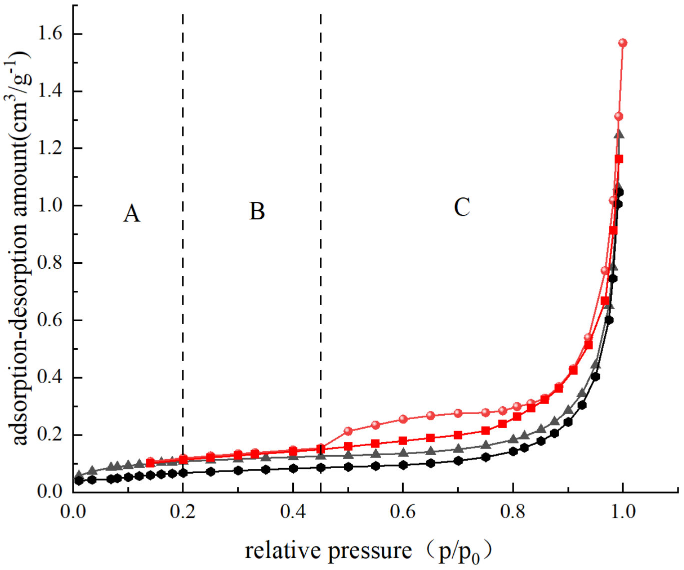

Figure 1. Isothermal adsorption-desorption curves before and after acidification

3.3 X-ray Diffraction

Research on the characteristics of the pore and fracture structure of coal before and after acidification indicates that after acidification, the minerals within the coal matrix are dissolved by the acid solution, resulting in an increase in both the specific surface area and volume of the pores. The composition of the coal matrix is the material basis that determines the extent of the space dissolution by the composite acid solution. Therefore, industrial analysis and X-ray diffraction (XRD) will be used to determine the changes in the types and content of minerals in the coal samples before and after acidification, to analyze and study the changes in the composition of the coal matrix before and after acidification.

Table 3. Industrial analysis before and after acidification

status	a(ml/g·r)	b(MPa^{-1})	Aad(%)	Mad(%)	Vad(%)	Fcad(%)
before acidification	23.597	0.483	29.3	0.43	25.26	67.34
after acidification	21.386	0.372	20.1	0.63	20.17	73.44

From Table 3, it is known that the coal sample’s ability to adsorb gas and the adsorption pressure are 1.103 and 1.31 times that of the acidified coal, respectively. The ash content is reduced from 29.3% to 20.1%, while the mass fraction of fixed carbon increases from 67.34% before acidification to 73.44% after acidification. This proves that the acidification process can effectively dissolve minerals in the coal, reducing the mass fraction of mineral matter and increasing the mass fraction of fixed carbon.

From Figure 2, it can be seen that the Camel Mountain coal sample is rich in minerals such as quartz (SiO_2), calcite ($CaCO_3$), kaolinite [$Al_2Si_2O_5(OH)_4$], and dolomite [$CaMg(CO_3)$]. After acidification with a composite acid solution, the diffraction intensities of calcite, dolomite, and kaolinite suddenly decrease, and most of the diffraction peaks of calcite and dolomite disappear. However, some quartz and kaolinite remain undissolved, indicating that the acid solution has a significant dissolution effect on calcite and dolomite in the Camel Mountain coal sample, but the effect on kaolinite and quartz is less satisfactory.

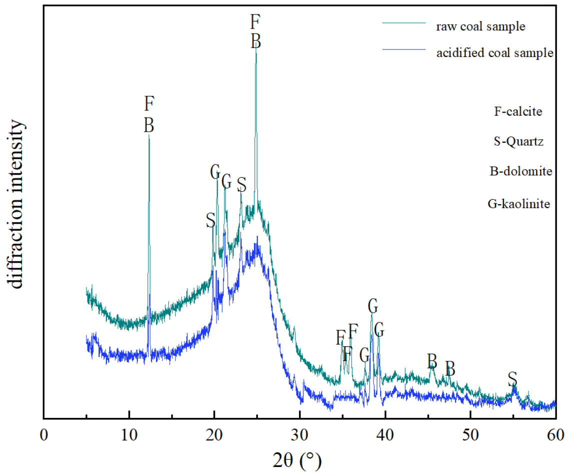

Figure 2. XRD patterns of coal samples before and after acidification

4. Conclusions

The factors affecting the acidification effect of low-rank coal from Camel Mountain Mine, in order of importance, are the mass concentration of HF, reaction temperature, mass concentration of HCl, and reaction time. The best acidification effect on the actual sample is achieved when the mass fraction of HCl is 6%, the mass fraction of HF is 9%, the reaction time is 6 hours, and the temperature is 35°C.

Through isothermal nitrogen adsorption experiments before and after acidification, as well as XRD diffraction experiments, it can be concluded that the dissolution of minerals in the coal leads to the formation of many etch pits and etch fractures on the surface of the acidified coal samples. The pores and fracture cracks are interconnected, improving the connectivity of the coal's pore and fracture system, which promotes the diffusion and migration of gas in the coal seam and is beneficial for enhancing the gas extraction rate. This indicates that the optimized acidification parameters have a good acid-etching effect on the minerals in high-rank coal.

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