

Study on the Change Law of Pore Structure and Permeability of Coal Under Chemical Permeability Enhancement Technology

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ABSTRACT

In order to deeply explore the permeability enhancement effect and permeability enhancement mechanism of the three chemical permeability enhancement technologies, the pore structure change and permeability enhancement mechanism of anthracite coal were studied from the perspective of coal pore structure. The following conclusions are drawn: the permeation effect of the four solutions from large to small is 99% CS₂, 10% NaClO, 8% HF, 8% HCl. The total pore volume of HCl and HCl solution decreases after acidification, the pore volume of HF solution increases after acidification, the number of pores in the coal sample after oxidation of NaClO solution increases, and the micropores are transformed into mesopores, and the pore volume of CS₂ solution increases after extraction, and the pore expansion effect is better than that of the other three solutions, and the pore volume with a pore diameter greater than 2 nm affects the flow of gas between pores, and the larger the pore volume, the higher the permeability. The pores with a pore diameter of less than 2 nm have little correlation with the permeability of coal and rock, and the micropores do not affect the gas flow.

KEYWORDS

Chemical permeability, pore structure, permeability.

1. INTRODUCTION

Complex geological reservoir conditions and low coal reservoir permeability in China: According to the statistics of 76 coal reservoir parameters in 23 representative target areas in China, the permeability of 72% of the reservoir areas is less than 1.0 mD, and low permeability is the main geological factor leading to the inefficient mining of coalbed methane in China^[1]. Therefore, solving the problem of low permeability of coal seams in China is very important for the efficient development of coalbed methane (gas). In recent years, the use of chemical methods to improve the permeability of coal seams has received extensive attention, mainly including acidification method, oxidation method, extraction method, etc. This technology changes the pore structure and surface properties of coal through the action of solvents, so that the porosity and permeability of coal seams increase. In order to compare the mechanism and permeability enhancement effect of the three chemical permeability enhancement technologies from the pore structure, the anthracite coal in Yuxi of Qinshui was modified, and the acidifiers hydrochloric acid (HCl) and hydrofluoric acid (HF), the oxidant sodium hypochlorite (NaClO), and the extractant carbon disulfide (CS₂) were selected for pore change analysis and permeability enhancement capacity test. The results of this study will provide an experimental basis for the chemical permeability enhancement and transformation of coal reservoirs.

2. EXPERIMENTAL PART

2.1. Experimental samples

The anthracite coal of No. 3 coal seam of Yuxi Coal Mine in Qinshui Basin was selected as the research object, and the results of industrial analysis of coal are shown in Table 1.

Table 1. Proximate analysis data of coal samples

Coal samples	Moisture/%	Volatile matter/%	Ash/%	Fixed Carbon/%
Yuxi coal	2.7	7.6	6.8	82.9

Table 2. Relative mass fraction of each mineral in coal

Sample number	Kaolinite/%	Calcite/%	Iron dolomite/%	Festilite/%	Quartz/%
raw coal	58.0	7.1	8.1	12.8	13.9
CS	57.0	7.8	8.6	12.5	14.1
HC	69.2	0.0	0.0	14.1	16.6
HF	0.0	0.0	0.0	0.0	0.0
NC	57.0	8.0	8.7	12.5	13.9

From Table 2, it can be seen that the content of raw coal kaolinite is the highest, and there are also high contents of fericite and quartz, as well as a small amount of calcite, iron dolomite and other minerals. After the dissolution of HCl solution, carbonate minerals such as calcite and iron dolomite disappeared, while silicate minerals such as fericite and kaolinite and quartz still existed. It can be seen that the main principle of acidification and permeability enhancement is to use acid to dissolve some mineral components to achieve the purpose of permeability. HCl solution is mainly used to dissolve carbonate minerals in coal samples, and HF solution can dissolve carbonates, silicates and quartz minerals in coal samples. Since the main components of minerals in the coal samples are silicate minerals and silica, the modification effect of HF solution is better than that of HCl solution. In the CS and NC coal samples, the contents of each mineral component did not change much from the raw coal, indicating that the CS₂ solution and NaClO solution did not dissolve the mineral components of coal and rock.

2.2. Experimental Methods

According to the national standard of "Preparation Method of Coal Sample" (GB/T474-2008), 12 coal pillars with a size of $\Phi 25$ mm \times 50 mm are cut by wire cutting machine. The prepared samples were dried at 80 °C for 24 h in a blast drying oven, and the coal samples were taken out after the temperature dropped to room temperature, and the permeability of the original coal pillars was tested. According to the permeability of the coal samples, they were divided into 4 groups and numbered according to the method of "solution-1, 2, 3". The numbered coal pillars were soaked in the corresponding solution for 6 h, dried and then tested for permeability. After the test, the raw coal and the modified coal samples were ground to below 200 mesh for infrared spectroscopy test. The modified coal samples of 8% HF solution, 8% HCl solution, 10% NaClO solution and 99% CS₂ solution were labeled as HF, HC, NC and CS, respectively.

In order to analyze the variation law of coal porosity under the action of different solvents, the pore structure of coal was tested by low-temperature liquid nitrogen adsorption method and CO₂ adsorption method, and the instrument used was the ASAP 2460 Version 3.01 adsorption instrument of Mack Company in the United States, and the experiment was carried out under the conditions of liquid nitrogen saturation temperature (77 K) and relative pressure (P/P₀) of 0.0001-0.9995.

The equipment used in this permeability test is TCQT-III. type low permeability coalbed methane phase displacement stimulation experimental device, the axial pressure of this experiment is set to 4 MPa, the confining pressure is set to 2 MPa, the inlet pressure is 1 MPa, and the test gas is nitrogen.

3. EXPERIMENTAL RESULTS

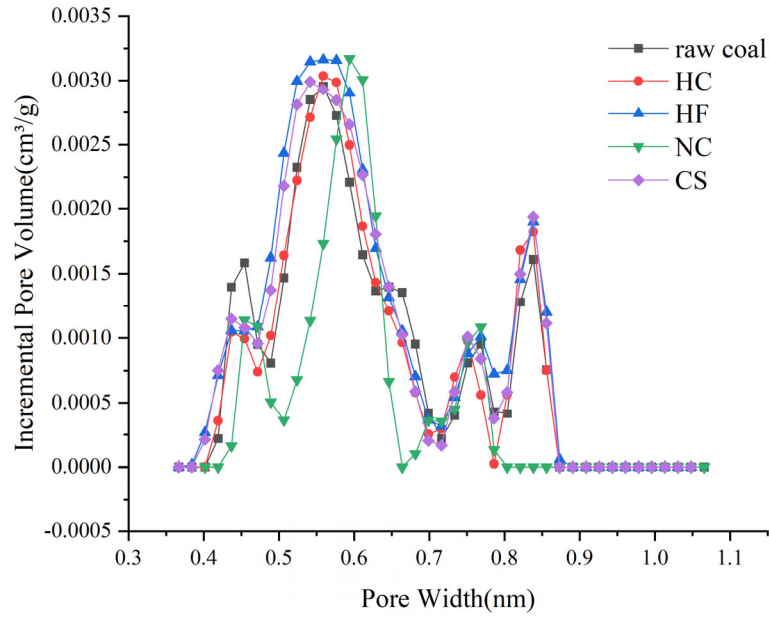
3.1. Changes in the distribution characteristics of coal pore size

According to the pore size classification method of the International Union of Pure and Applied Chemistry (IUPAC), the pores in coal can be divided into microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm). In order to make the pore size distribution data more intuitive, the tested pore size was divided into three parts, among which V₁ was the pore volume of micropores (pore size of <2 nm), V₂ was the pore volume of medium pores (pore size 2-50 nm), and V₃ was the pore volume of macropores (pore size > 50 nm).

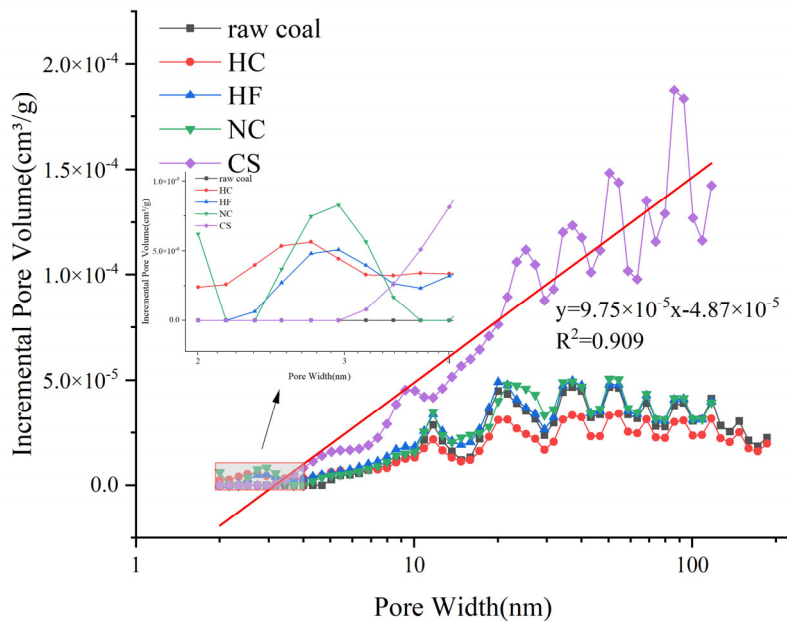
Table 2. Pore size distribution parameters

Coal samples	V ×10 ⁻⁴ cm ³ /g	Stage pore capacity (×10 ⁻⁴ cm ³ /g)			Stage hole volume ratio (%)		
		V ₁	V ₂	V ₃	V ₁	V ₂	V ₃
raw coal	347.83	335	7.02	5.81	96.31	2.02	1.67
HC	339.56	329	5.79	4.77	96.89	1.71	1.40
HF	413.6	399	8.4	6.2	96.47	2.03	1.50
NC	230.43	216	8.46	5.97	93.74	3.67	2.59
CS	366.71	329	19.83	17.88	89.72	5.41	4.88

Table 2 and Figure 1 show that micropores dominate the pore volume distribution at each stage, accounting for about 55% of the total pore volume. The raw coal samples are mainly silicate minerals (kaolinite, fermanite), but also carbonate minerals (calcite, ferrodolite) and quartz. The total pore volume of the coal sample decreased by 2.37% after treatment with HCl solution, indicating that the clay mineral kaolinite swelled after hydrochloric acid acidification, resulting in a decrease in the total pore volume. The total pore volume of HF coal samples increased by 18.91% after the coal sample was treated with HF solution, indicating that HF solution had a better pore expansion effect than HCl solution, so that the mineral components in the pores could be fully dissolved without being affected by the expansion of clay minerals. Therefore, the influence of carbonate minerals and clay minerals on coal samples should be considered when selecting acidifiers for permeability. After treatment with NaClO solution, the total pore volume content in NC coal samples decreased by 33.75%, mainly due to the decrease of micropore volume, while the pore volume of medium and macroporous pore volume increased. After being treated with CS₂ solution, the total pore volume of CS coal samples increased by 5.43%, of which the medium pores increased by 182.48% and the macropores increased by 207.75%.



(a) Small holes



(b) Mesopores and macropores

Figure 1. Pore volume distribution

3.2. Permeability changes

In order to better reflect the influence of different solutions on the permeability of coal samples, the concept of permeability β is used to represent the transformation effect. The changes in permeability of coal samples before and after dissolution are shown in Table 3.

$$\beta = (K_2 - K_1) / K_1 \times 100\% \quad (1)$$

where: β is the permeability rate, %; K_2 is the permeability of the coal sample after extraction, mD, and K_1 is the permeability of the coal sample before extraction, mD.

Table 3. Comparison of permeability of coal samples before and after treatment

Sample number	Permeability before dissolution/mD	Permeability after dissolution/mD	Permeability rate/%
CS ₂ -1	0.002204	0.320037	14421
CS ₂ -2	0.008440	0.418591	4860
CS ₂ -3	0.015016	1.025220	6728
HCl-1	0.002410	0.003118	29
HCl-2	0.007350	0.007385	0
HCl-3	0.024832	0.027809	12
HF-1	0.002765	0.004396	59
HF-2	0.006712	0.014461	115
HF-3	0.010813	0.053807	398
NaClO-1	0.004137	0.016971	310
NaClO-2	0.005566	0.017653	217
NaClO-3	0.014495	0.072287	399

As can be seen from Table 2, the permeation effect of the four solutions was different, and the average permeation effect of each solution was 8669.7% for CS₂ solution. NaClO solution: 308.7%; HF solution: 190.7%; HCl solution: 13.6%. Among the three types of permeability, the permeability of the CS₂ solution by extraction is an order of magnitude higher than that of the NaClO solution by the oxidation method and the HCl solution and the HCl solution with the HF solution by the acidification method. This results show that the extraction method of CS₂ solution can effectively modify the coal structure, expand the seepage channel, and facilitate the flow of experimental gas^[2]. The poor effect of HCl solution modification, and even the permeability increase rate of a group of 0%, may be due to the fact that the fractures modified by HCl solution are closed under confining pressure, resulting in poor permeability enhancement effect, and the coal dust and acidified precipitate produced after acidification will also affect the permeability^[3]. Other solutions will also be affected by confining pressure after transformation, but the impact is less because the transformation effect of other solutions is better.

4. DISCUSS

In order to better compare the relationship between pore volume and permeability, the concept of capacitization α is used to represent the effect of solvent pore expansion and expansion, as shown in Equation 2:

$$\alpha = (V_2 - V_1) / V_1 \times 100\% \quad (2)$$

where α is the expansion rate, %; V_2 is the pore volume of the coal sample after soaking, cm^3/g , and V_1 is the pore volume of the coal sample before soaking, cm^3/g .

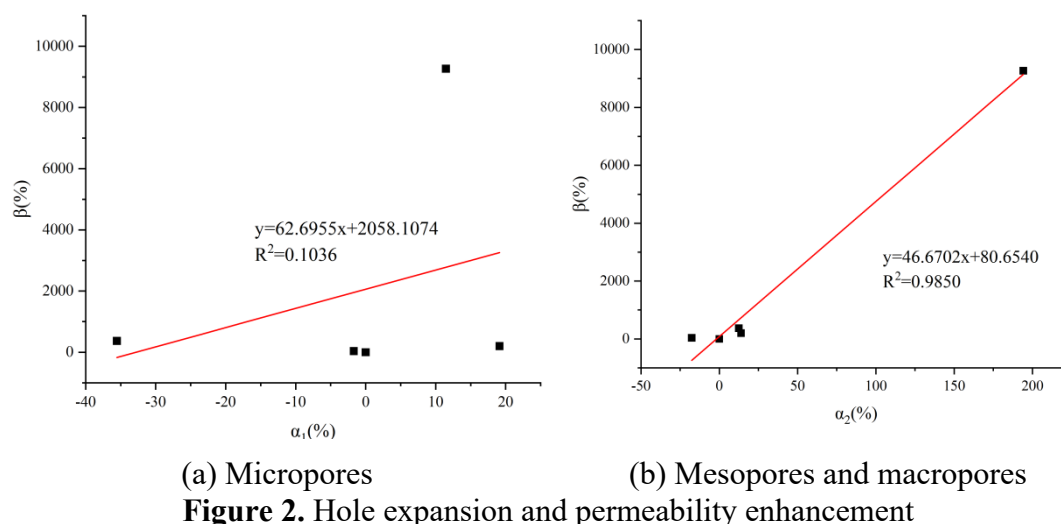
The pore expansion rate of the pore size less than 2 nm measured by the CO_2 adsorption experiment was recorded as α_1 , and the pore expansion rate of the pore size greater than 2 nm measured by the low-temperature liquid nitrogen adsorption experiment was recorded as α_2 . The expansion rate and permeability of each solvent are shown in Table 4.

Table 4. Expansion rate and transparency increase rate

Coal samples	$\alpha_1/\%$	$\alpha_2/\%$	$\beta/\%$
HC	-1.71	-17.63	35
HF	19.12	13.88	199
NC	-35.55	12.48	369
CS	11.46	194.15	9269

In order to clarify the correlation between the pore volume of coal samples and the permeability of coal and rock, the relationship between the expansion rate and the permeability of each coal sample after solvent treatment was drawn and linearly fitted. Figure 2(a) shows the relationship between the micropores and the permeability of the coal sample measured by CO_2 adsorption. As can be seen from the figure, there is no significant correlation between the pore volume and the permeability of the sample, because in the pores with a pore size of less than 2 nm, the gas is adsorbed on the pore surface in the form of adsorption and does not participate in the seepage of the gas in the pores. Fig. 2(b) shows a positive correlation between mesopores and macropores and permeability measured by cryogenic liquid nitrogen adsorption experiments. As can be seen from the diagram. With the increase of pore volume, the permeability of coal and rock also increases^[4], and the correlation coefficient R^2 is 0.9850. This indicates that the increase of the pore volume of macropores enhances the connectivity between the pores, which is conducive to the seepage of gas in coal and rock.

In specific experiments, the expansion effect of HF solution for pores with pore size greater than 2 nm was higher than that of NaClO solution, but the permeabilization effect of NaClO solution was higher than that of HF solution. This indicates that the improvement of the seepage capacity of coal and rock is not only related to the pore porosity, but also affected by other factors such as pore morphology and functional groups in the coal.



5. CONCLUSION

(1) The permeability enhancement effects of the four solutions on Qinshui Yuxi coal were 99% CS₂ solution, 10% NaClO solution, 8% HF solution and 8% HCl solution. The average permeabilization rate of the 99% CS₂ solution was 9269%, which was much higher than that of the other three solutions. The average permeability increase rate of the three coal samples after HCl transformation was 35%, and the permeability increase rate of one coal sample was 0%, and the transformation effect was poor.

(2) Before and after solution treatment, the pore volume with a pore diameter greater than 2 nm affects the flow of gas between the pores, and the larger the pore volume, the higher the permeability. The pores with pore size less than 2 nm have little correlation with the permeability of coal and rock, and the micropores do not affect the flow of gas. Pore volume is not the only factor affecting the permeability of coal and rock.

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