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Experimental research on displacing coal bed methane with supercritical CO_2 ☆

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A B S T R A C T

The high-gas and low-permeability are the common problems of China coal mine, which restrain the mining of coal-seam gas resources safely and efficiently. Hence, to solve the problem of low permeability of coal seam, an experimental system was set up and experimental research was conducted to investigate the effect of the displacement of methane by injecting supercritical CO_2 into coal samples. The experimental results indicated that, the extraction effect of supercritical CO_2 changes the coal's porosity, and broadens the seepage channel for methane. Thus, the methane could be desorbed effectively from the coal matrix, and flow through more cracks at higher speed.

1. Introduction

China ranks the third place by boasting of 98.9 billion tons exploitable coal in the world. Meanwhile, the country is abundant in coalbed methane at 36.7 trillion m^3. However, these coal seams are generally characteristic of low-permeability, so it is difficult to extract the methane and hence the drainage effect is very poor (Zhou, 1990; Sun, 2003). This is not beneficial to the drainage of coalbed methane and the prevention of gas accidents. Increasing the production capacity of coalbed methane becomes one of the key technologies in the methane drainage process. Therefore, plenty of researches (Clarkson and Bustin, 2000; Zuber, 1998; Reznik et al., 1984; Cheng, 2001; Wu and Guo, 2001; Tang et al., 2004a,b; Sun and Liang, 2005; Goodman, 1977; Brooks and Smith, 1967) on the improvement of drainage efficiency of the coalbed methane had been conducted at home and abroad. And gas injection is one of the main methods to increase the methane production. Generally speaking, increasing methane by gas injection is mainly due to the driving and fracturing effect, reduction of pressure effect, the competition adsorption function and the filtering adsorption effect (Wu, 2009).

Supercritical CO_2 (abbreviated as "SC-CO_2") is a kind of supercritical fluid. Supercritical fluid extraction technology has been a state-of-the-art chemical separation technology that gained rapid development internationally in the past twenty years (Zhu, 2007; Zhang, 2002; Stahl et al., 1978; Randall and Bowman, 1982; Moyler, 1993). The viscosity of supercritical fluid is close to that of gas, and the diffusion coefficient is between gas and liquid. It not only has the advantage of liquid characteristic of large solubility, but also the property of gas that is easier to spread and move. Moreover, the dissolving capacity of supercritical fluid increases with the liquid density. The critical temperature (T_c) and critical pressure (P_c) of carbon dioxide are 31.06 °C and 7.39 MPa, respectively, and its critical density ρ (0.448 g/cm^3) is the highest among common used supercritical solvents. Therefore the critical data demonstrate that carbon dioxide is the most suitable supercritical solvent. Moreover, low cost and no pollution, etc. make it the most popular supercritical fluid used for extraction. Since in the process of increasing production by gas injection to coal-bed methane, carbon dioxide is mostly in a supercritical state. The literature (Stahl et al., 1978) raised that the lower-polarity hydrocarbons and lipid organic compounds can be extracted in the lower pressure range (7–10 MPa). Therefore, it is of great significance to research the SC-CO_2 injection into coal seam for improving the drainage of coal-bed methane.

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2. Experimental method

2.1. Coal sample

The coal sample used in the SC-CO_2 displacement experiment was collected from Zichang Coal Mine of Shanxi Province. It is a kind of low-permeability coal seam, and the industrial analysis data of it are listed in Table 1.

The coal sample shown in Fig. 1 was processed into the standard cylinder specimen of $\varphi 50 \times 100$ mm, and its surface on both ends was polished to meet the laboratory precision.

2.2. Experimental equipment

The equipment used in the SC-CO_2 displacement experiment was developed by ourselves, and it can be used to test the permeability of coal sample. Fig. 2 shows the equipment's mechanism schematic diagram, and the physical picture is showed in Fig. 3.

In the CH_4 displacement experiment with SC-CO_2, a big problem is how to separate CO_2 and CH_4, and then how to calculate the volume of CH_4 flowing out. From related literatures, it can be known that CO_2 and the NaOH solution easily react each other and generate Na_2CO_3 or $NaHCO_3$. The solubility of NaOH is 109 g at room temperature. The CO_2 could be collected sufficiently if the appropriate concentration of NaOH is calculated by the chemical equation. Therefore, the NaOH aqueous solution was selected as the separating liquid. We lengthened the reaction pipeline to ensure the reaction was adequate.

2.3. Experimental process

The displacement experiments include gas adsorption, desorption experiment and the CH_4 displacement with SC-CO_2. To validate the effect of the SC-CO_2 displacement experiment to the coal permeability, the permeability of coal samples before and after the displacement experiment was measured, respectively. The permeability test, gas adsorption experiment and desorption experiment were carried out at room temperature, while the experimental temperature of CH_4 displacement experiment with SC-CO_2 is at 50 °C.

2.3.1. Permeability test

Before the displacement experiment, the processed raw coal sample was placed into the triaxial seepage equipment firstly, and then the reaction kettle was sealed. Meanwhile, the air tightness was examined to ensure its good condition after connecting all the pipelines and instruments. Finally the axial compression and confining pressure were alternately increased slowly, but the former is a little larger than the latter. And then pore pressure was enhanced. The pore fluid used in the permeability test is nitrogen. The drainage method for collecting gas was adopted to measure the gas output. When the water flowed steadily, the volume of effluent fluid was measured in a certain time frame, and record the experimental data. This procedure was repeated three times under the same pressure combination. Once the pressure was adjusted, the data were tested only if the flow kept stable to ensure that the former process has no influence on the flowing process. After finishing the original permeability test, the axial compression and the confining pressure were decreased alternately to prevent the sample from being destroyed. Then the CH_4 displacement experiment with SC-CO_2 was conducted.

After the CH_4 displacement experiment with SC-CO_2 was finished, the influence of temperature to the permeability test of the specimen was eliminated. The permeability test was repeated by steps until the temperature of the reaction kettle dropped to the ambient temperature. The data were recorded, then the permeability changes of the coal were calculated and analyzed before and after supercritical CO_2 experiment.

Fig. 1. Coal sample used in displacement experiment.

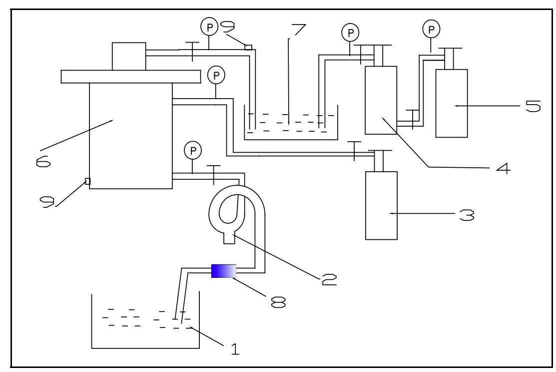

Fig. 2. The schematic diagram of SC-CO_2 displacement experiment system. 1 – Gas gathering device; 2 – product separation device; 3 – confining pressure cylinders; 4 – high pressure CO_2 cylinders; 5 – CO_2 fill cylinders; 6 – displacement experiment reaction axe; 7 – CO_2 preheating and heat preservation device; 8 – gas accumulated flowmeter; 9 – temperature sensor.

Fig. 3. The experiment system of SC-CO_2 displacing coalbed methane.

Table 1
The industrial analysis data of coal from Zichang.

Sample	Aad%	Mad%	Vad%	FCad%
Coal of Zichang	10.68	2.56	30.68	56.08

2.3.2. Gas adsorption experiment

To quantify the effect of SC-CO_2 displacing CH_4, the processed specimen was put into the response instrument. The axial compression and the confining pressure were fixed at 10 MPa and 9 MPa, respectively, and the pressure values were made the same as the stabilizer. The inlet valve of the osmotic pressure was closed, and then the gas outlet of reactor axe was connected with vacuum pump. Afterwards, the vacuum was extracted for 8 h, then the outlet valve was closed and the vacuum pump was dismantled. Finally, the pore pressure valve was opened, and the CH_4 whose concentration and pressure were 99.9% and 4.7 MPa infused separately. Meanwhile, the pressure and time were recorded until the gas pressure did not change any more.

2.3.3. Gas desorption experiment

After the adsorption experiments, the axial compression and the confining pressure of the osmoscope were kept unchanged. The inlet of the pore pressure was closed, and the outlet of the reaction kettle was opened. Simultaneously, the gas desorbed by drainage was collected. The time and volume were recorded together. The experiment ended until the gathered gas volume no longer changed.

2.3.4. CH_4 displacement with SC-CO_2

In this experiment, the temperature was fixed at 50 °C and the pressure of carbon dioxide at 8.0 MPa. First of all, all the equipments and instruments were adjusted, the circular heating water was heated to 50 °C in the temperature control heater. The temperature was kept constant. Meanwhile, the reaction kettle and all pipelines were ensured in good heat insulation.

Then, the control valve of pore pressure and the reaction kettle outlet was opened slowly. Subsequently, the SC-CO_2 was injected. The mixture of CO_2 and CH_4 flowed out from the outlet. The fixture was collected by drainage limewater after passing the gathering system. In addition, the time and the gas volume were recorded. During the process, the temperature and pressure were maintained to be the set values. The experiment was stopped until the clear limewater turned turbid.

3. Results of the displacement experiment

3.1. Displacement efficiency

The calculation indicated that the total volume of the gas adsorbed was 4722.56 ml, that is, the gas volume adsorbed by the coal is 3882.56 ml after the natural desorption.

The experimental result of the SC-CO_2 displacing gas is shown in Fig. 4, which illustrates that at the beginning there is a larger gas output with a high speed. As the time lapses, the gas output decreases slowly until almost no gas flows out.

From the results, it can know that, in the early phase, the gas replaced is mainly the free gas which is contained in the seepage channels composed of pores and cracks. While the decline of gas output is mainly due to the replacement and displacement of SC-CO_2, which can desorb CH_4 from the adsorption state. Finally, the desorbed CH_4 flows to the seepage channel, and runs out from the sample along with the airflow.

According to the adsorption and desorption experiments, it is calculated that the total volume of gas adsorbed V_1 is 4722.56 ml, and the accumulative volume of gas collected in the displacement experiment V_2 is 3674 ml.

The displacement efficiency is represented as η, and is defined as follows:

$$\eta = \frac{V_2}{V_1} \times 100\% \quad (1)$$

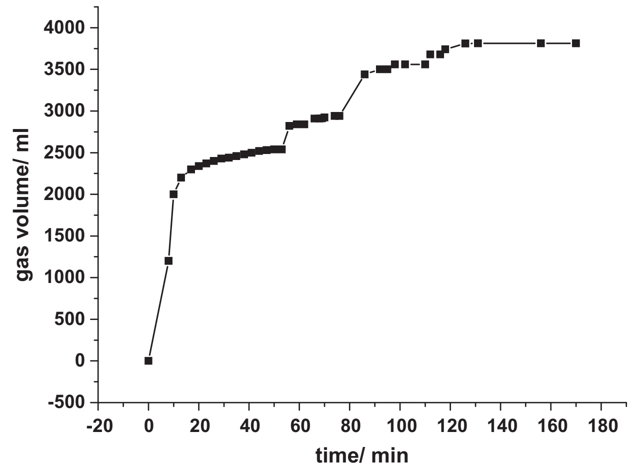

Fig. 4. The relationship of gas output variation with time.

where V_1 – the total volume of gas adsorbed in the adsorption experiment; V_2 – the accumulative gas volume collected in the displacement experiment.

Put the values of V_1, V_2 into Eq. (1), the displacement efficiency is 77.8%. It demonstrates that the experiment achieves a good result.

3.2. Analysis of the results

The process of SC-CO_2 displacing CH_4 can be divided into two parts: one, as a kind of competitive gas, the SC-CO_2 competes with CH_4 to be adsorbed in the coal. Since the coal has a bigger absorption ability to CO_2 than that of CH_4, some CH_4 will be replaced in the displacement process; two, while SC-CO_2 flows through the coal, SC-CO_2 could also extract part of organic matters in the coal. According to the dissolution law of SC-CO_2 studied by Stahl et al. (1978) and the extraction principle of supercritical fluid, it can be concluded that when the SC-CO_2 acts on the coal, the hydrocarbon of lower polarity and lipid organic compounds in the coal, such as esters, ethers, lactones, and epoxy compounds, could be extracted in the lower pressure range between 7 and 10 MPa.

As shown in Fig. 5, more cracks were made by the experiment and the penetration of coal under the stress was to be affected by the result.

Figs. 6 and 7 show the variation of the permeability with the volume stress of Zichang coal before and after the SC-CO_2 experiment. In Fig. 5, while the pore pressure remains unchanged, the permeability of the coal decreases as the volume stress Θ increases because the fixed pore osmotic pressure P hints that the deformation of the solid skeleton and the expansion degree of pore are

Fig. 5. The coal sample used in displacement experiment.

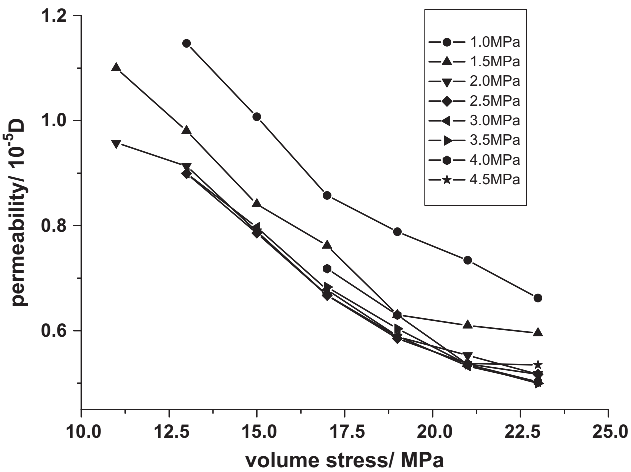

Fig. 6. The relationship between the permeability and the volume stress of Zichang coal sample before the supercritical experiment.

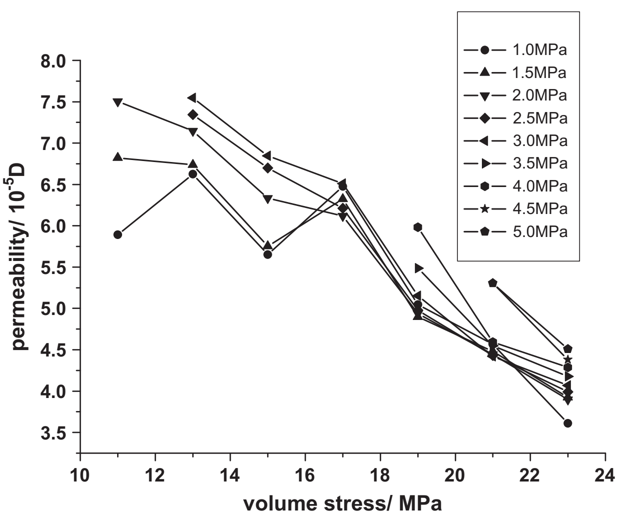

Fig. 7. The relationship between the permeability and the volume stress of Zichang coal sample after the supercritical experiment.

fixed. As the volume stress Θ increases, the effective stress σ_0 acting on the coal will also increase that prompts the contraction distortion of the coal. Simultaneously, the porosity and expansion degree of the crack will decrease, even some cracks will close. These combined change the microstructure of the coal. Moreover, the effective fluid seepage channels become lesser. Finally, the value of the permeability k reduces.

In Fig. 7, there shows significant difference in the relationship between the permeability and the volume stress Θ and the pore pressure p after the SC-CO_2 extraction experiment. It may be because the SC-CO_2 extraction experiment generates plenty of pores and cracks in the coal. When the pore pressure is relatively small (e.g.: p = 1.0 MPa, p = 1.5 MPa or p = 2.0 MPa), the curve fluctuates with the increasing of the volume stress, and the fluctuation becomes more and more unobvious as the pore pressure increases. Finally, there will be no fluctuation when the pore pressure grows to a certain value. Because the SC-CO_2 displacing CH_4 experiment influences the coal structure, and the pore and crack system will experience a series of complicated changes under the combined action of the volume stress and the pore pressure. When the value of the pore pressure is relatively small, its influence on the expansion degree of cracks is limited. Thus, the variation of the permeability with the volume stress is not substantial in low pore pressure area. This is a remarkable feature found in this experiment study.

4. Conclusions

The SC-CO_2 displacing CH_4 experiment achieves good results, and the displacement efficiency can reach 77.8%. It is proved that the production of coal-bed methane will be improved through injecting SC-CO_2 to the high-gas and low-permeability coal seam. This provides a new method for the drainage of coal-bed methane and the prevention of gas accidents.

The permeability achieves a good improvement after the SC-CO_2 effecting on the coal. It is because the SC-CO_2 extraction experiment generates plenty of pores and cracks in the coal. It lays a solid foundation for the improvement of the permeability and the gas drainage efficiency.

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