Experimental Study on the Adverse Effect of Gel Fracturing Fluid on Gas Sorption Behavior for Illinois Coal

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Experimental study on the adverse effect of gel fracturing fluid on gas sorption behavior for Illinois coal

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Abstract: Hydraulic fracturing is an effective technology for coal reservoir stimulation. After fracturing operation and flowback, a fraction of fracturing fluid will be essentially remained in the formation which ultimately damages the flowability of the formation. In this study, we quantify the gel-based fracturing fluid induced damages on gas sorption for Illinois coal in US. We conducted the high-pressure methane and CO₂ sorption experiments to investigate the sorption damage due to the gel residue. The infrared spectroscopy tests were used to analyze the evolution of the functional group of the coal during fracturing fluid treatment. The results show that no significant chemical alteration of coal due to the fracturing fluid injection, and the damage of sorption is attributed to the physical blockage and interactions. As the concentration of fracturing fluid increases, the density of residues on the coal surface increases and the adhesion film becomes progressively denser. The adhesion film on coal can apparently reduce the number of adsorption sites for gas and lead to a decrease of gas sorption capacity. In addition, the gel residue can decrease the interconnectivity of pore structure of coal which can also limit the sorption capacity by isolating the gas from the potential sorption sites. For the low concentration of fracturing fluid, the Langmuir volume was reduced to less than one-half of that of raw coal. After the fracturing fluid invades, the desorption hysteresis of methane and CO₂ in coal was found to be amplified. The impact on the methane desorption hysteresis is significantly higher than CO₂ does. The reason for the increasing of hysteresis may be that the adsorption swelling caused by the residue adhered on the pore edge, or the pore blockage caused by the residue invasion under high gas pressure. The results of this study quantitatively confirm the fracturing fluid induced gas sorption damage on coal and provide a baseline assessment for coal fracturing fluid formulation and technology.

Key words: Hydraulic fracturing, coal, gas sorption, desorption hysteresis

Highlights:

- Intrusion of residue significantly reduces the pore volume of the coal
- Evaluation of influence of gel fracturing fluids on gas sorption and diffusion
- The effect of different concentrations of gel fracturing fluids on the pore structure of coal
- No significant chemical reaction occurs between fracturing fluids and coal

1.Introduction

Gas production from coal cannot only provide clean energy, but improve the safe mining when coal is being mined (Yuan 2016; Cao et al. 2017; Tian et al. 2020). Coal is known as its low permeability due to its tight structure (Liu and Harpalani 2013; Zhai et al. 2016). Hydraulic fracturing is widely used in the coalbed methane (CBM) extraction (Montgomery and Smith 2010; Cao et al. 2017; Xu et al. 2017). In hydraulic fracturing operation, the high-pressure proppant-carrying fluid is injected into the coal formation and the proppants are trapped in the CBM fracture system to maintain high permeability pathway after the flowback (Ma et al. 2017; Lv et al. 2018; Zhai et al. 2018; Zhi et al. 2018). In CBM fracturing, fracturing fluids commonly used can be divided into slick water and gel (Li et al. 2016; Thombare et al. 2016). In recent years, the viscoelastic surfactants containing fracturing fluids have been considered for applications (Lu et al. 2015). In CBM fracturing jobs, 20% ~ 30% of the injected fracturing fluid was observed to be permanently retained in the reservoir from the field observations (Palmer et al. 1991; Al-Ameri et al. 2018; Huang et al. 2021).

The fracturing fluid residues may have a series of effects on the reservoir flow deliverability due to physical blockage of flow pathway (Huang et al. 2020). In addition to the damage of permeability, the residual fracturing

fluid may significantly modify the surface property of coal which will ultimately change sorption and diffusion behaviors of coal (Yang et al. 2019; Liu et al. 2019). Chen et al. observed that the degree of influence of fracturing fluid on the adsorption of methane in CBM formation is closely related to coal rank, and Lean coal has the greatest influence among coking coal, lean coal and anthracite (Chen et al. 2009). The fracturing fluid can reduce the diffusivity of coal and the fracturing fluid as the absorbate can absorb a certain amount of gas (Kang et al. 2016). You et al. compared the performance and mechanism of anionic surfactants and cationic surfactants in the formulation of clean fracturing fluids to inhibit methane desorption (You et al. 2015). Interestingly, Lu et al. found that the clean fracturing fluid can eliminate the clay minerals in the pores through chemical reactions, thereby widening the pores for gas flow (Lu et al. 2017). When different types of fracturing fluids were applied on the coal surface, different contact angles were observed and they therefore have different influence on desorption and diffusion of methane in the coal (Chen et al. 2009). Additionally, CO₂ is often used as an additive, mixed with gel or surfactant to prepare fracturing fluid to improve fracturing performance in recent years (Jing et al. 2014; Li et al. 2020). It can be inferred that the solid or liquid residues of the fracturing fluid may also cause changes in the adsorption and desorption

of CO₂ in the coal, thereby affecting the final fracturing stimulation effect. There are differences in the adsorption and mechanism of methane and CO₂ in coal (Zhang and Liu 2017; Cheng et al. 2018). Therefore, the influence of fracturing fluid residues invading to the coal on CO₂ adsorption may also be different from that on methane adsorption. However, there are very few experimental studies on the impact of hydraulic fracturing on the flowability of CO₂ in coal seam.

Gas desorption is the first stage of the gas migration process in coal mine gas drainage process. We use the coal sample from the Illinois Basin in the United States as testing samples and explore the influencing characteristics and mechanism of the gel fracturing fluid on the methane and CO₂ ad-/desorption behavior. The finding of this study can provide a baseline reference for the optimization and improvement of coal seam fracturing fluid blending towards final effective formation stimulations.

2 Preparations of coal samples and fracturing fluids

For the CBM fracturing fluid additives, we chose the following additives and level for our experiments. We use hydroxypropyl guar (HPG) cellulose as the thickener and four concentrations were proposed and they are 0.2%, 0.4%, 0.8%, 1.2% (weight percent). The organoboron was chosen as the cross-linking agent with a concentration of 0.4% and the potassium chloride (KCl) as the anti-swelling agent with a concentration of 1.5%. For fracturing fluid preparation, the following detailed procedure was followed: (1) keep the well-mixed water in the beaker at room temperature; (2) add 1.5% KCL as anti-swelling agent to the beaker; (3) add all targeted additives and stir to make it completely dissolved; (4) finally, let it stand until the bubbles in the prepared fluids gradually rise and disappear. All the prepared fluids were then stored at the environmental chamber for future coal sample

treatments.

For the sorption experiments, Illinois (IL) basin high-volatile bituminous coal samples were used. The fresh coal blocks were collected from the Illinois No. 6 coal seam from southern Illinois region in USA. Coal was pulverized and screened to 60 to 80 mesh (0.25 to 0.18 mm). We partitioned the coal sample into several portions with each portion of ~ 50 grams.

For the coal sample treatment, ~500 g of each fracturing fluid was used to treat ~50 g of coal sample for ~5 days. To allow well mixing, the fluid and sample were stirred for 5 minutes for each day. After 5-day treatment, the coal samples were dried at 60 °C. Both raw and treated coal samples were tested for gas sorption experiments for both methane and CO₂. To check whether chemical structure of coal altered or not due to fracturing fluid treatment, infrared spectroscopic analyses were used to probe coal samples before and after treatment.

3 Gas sorption experiments and modeling

All gas sorption experiments were carried out using the HPT-SDVS sorption system, manufactured by UNGES LLC, USA. Fig. 1 shows the schematic and photo of the HPT-SDVS sorption system. The system includes a reference cell and a sample cell which are used for quantifying the Gibbs gas storage capacity. The whole system was placed in a high accurate water bath for constant gas sorption. We conducted all our sorption experiments at 30°C. Before injecting gas, vacuum pump is used to vacuum the reference cylinder, sample cylinder and gas injecting system. The gas was injected into the system in a step-wised manner until the final pressure. The equilibrium was achieved before the next testing pressure. The Gibbs and absolute gas sorption amounts were calculated for each testing pressure, which are used for the gas sorption isotherm establishment.

Fig. 1 HPT-SDVS sorption system in the lab.

Gas adsorption kinetics is important for the gas storage modeling and many mathematical representations of gas sorption isotherms have been proposed and used, including Langmuir model, BET model, D-R model and D-A model (Yang et al. 2019; Dutta et al. 2008). The Langmuir model is an sorption model based on the monolayer sorption theory (Equation 1). Because of its simplicity, Langmuir model is the most widely used mathematical representation for gas sorption on coal (Levy et al. 1997). In this study, the Langmuir model was used to analyze the sorption data:

$$V_{Gibbs} = \frac{V_L P}{P_L + P} \quad (1)$$

where, V_{Gibbs} is the Gibbs sorption capacity, mL/g; V_L is the Langmuir volume, which represents the limit adsorption capacity of the coal sample for methane, mL/g; P_L is the Langmuir pressure, representing the half of the equilibrium pressure of the gas corresponding to the limit adsorption capacity, MPa.

The total gas sorption capacity should be represented by the absolute sorption volume. The occupied adsorbed phase should be corrected based on the Gibbs sorption capacity. Sudibandriyo et al. proposed the calculation formula of absolute adsorption (Li et al. 2019):

$$V_{abs} = \frac{V_{Gibbs}}{1 - \frac{\rho_{gas}}{\rho_{ads}}} \quad (2)$$

where, V_{abs} is the absolute adsorption capacity, ρ_{gas} and ρ_{ads} are the gas phase and adsorption phase density. For methane, its adsorption phase

density is 0.421 g/cm^3 , which is an assumption that the adsorbed gas is of liquid phase density. Under different pressure conditions, the density of methane is not the same, which can be calculated by the Peng-Robinson equation (Sudibandriyo et al. 2003).

4. Microscopic surface observation and infrared spectroscopy analyses of tested coals

The fracturing fluid may form colloid clusters to physically cover the sorption sites and modify the sorption characteristics of coal. It is also possible that the chemical additive of fracturing fluid can potentially react with the coal surface functional groups and radicals of coal to alter the sorption behavior of coal. To investigate the physical coverage of fracturing fluid, we used a digital microscope to observe and analyze the surface of each group of coal samples (Fig. 2).

To quantify the chemical surface property evolution, Fourier Transform Infrared Spectrometry (FTIR) was used to measure the changes in the surface functional groups of the coal sample before and after fracturing fluid treatment. This experiment uses Bruker VERTEX 80v infrared spectrometer, and the probing spectrum ranges from 8000 to 350 cm^{-1} .

Fig. 2 Microscopic coal surface fracturing fluid observations.

In FTIR experiment, $\sim 0.5 \text{ mg}$ coal samples were selected for testing. In each test, a small amount of potassium bromide was added for soaking and then the sample was pulverized down to 200 mesh. The pulverized sample was then compressed into a thin sheet with a

thickness of 0.1 to 1 mm for FTIR measurement. After obtaining the infrared spectrum of each sample, each peak was classified and analyzed to compare the chemical shifts.

Fig. 3 Methane sorption isotherms of IL raw coal

Fig. 3 shows methane adsorption and desorption isotherms for IL raw coal. There is no apparent desorption hysteresis for raw coal. **Fig. 4** shows the sorption isotherms with different fracturing fluids treatments. It is apparent that the fracturing fluid treatments significantly

reduce the methane gas sorption capacity with comparison between **Figs. 3 and 4**. Among the 4 groups of treated coal samples, the sorption capacities are somewhat similar. It is worthwhile to mention that the high levels of HPG (0.8% and 1.2%) can lead to a noticeable desorption hysteresis as illustrated in **Fig. 4**.

5 Result analyses and discussion

5.1 Adsorption and desorption characteristics of coal sample treated by fracturing fluid

Figs. 3 to 6 show the experimental data of adsorption and desorption isotherms for all tested coal samples. Overall, Langmuir model can describe the sorption behaviors within the tested pressure range. This confirms that the Langmuir model can be used to define the sorption capacity and pressure relationship when pressure is up to ~ 8 MPa.

c

d

Fig. 4 Methane ad-/desorption isotherms of coal treated by fracturing fluids with different HPG concentrations

As expected, the CO₂ sorption capacity is much higher than methane if we compare Figs. 3 and 5. Similar to methane sorption, the CO₂ sorption capacity decrease after the fracturing fluid treatments as illustrated in Figs. 5 and 6. To quantitatively analyze the influence of fracturing fluid on the sorption of methane and CO₂ on IL coal, the Langmuir volumes were estimated and compared in Fig. 7. The Langmuir volume represents the ultimate gas adsorption capacity of coal, that is, the larger the Langmuir volume, the stronger the gas adsorption capacity of coal at the infinite pressure. From Fig. 7, it was found

that the Langmuir volume of the IL coal for CO₂ adsorption is 42.5 mL/g, which is almost twice of methane adsorption of 22.2 mL/g. It can be seen from Fig. 7a that after the fracturing fluid treatment, all methane Langmuir volumes dropped below 10 mL/g, which is less than one-half of the raw coal. The Langmuir volumes of coal samples treated with 0.8% and 1.2 % were slightly lower than those treated with 0.2 % and 0.4 % fracturing fluid suggesting that high concentration fracturing fluid would cause more damage to the coal sorption capacity.

Fig. 5 CO₂ ad-/desorption isotherm of raw coal

a

b

Fig.6 CO₂ ad-/desorption isotherms of IL coal treated by fracturing fluids

Fig. 7 The ad-/desorption Langmuir volume of each group of coal samples

To quantitatively evaluate the fracturing fluid induced sorption damage, this study introduces a concept of sorption damage factor (α) as described as:

$$\alpha = \frac{V_{L0} - V_{Lr}}{V_{L0}} \times 100\% \quad (3)$$

where, V_{L0} is the volume of Langmuir absorbed by the raw coal, and V_{Lr} is the Langmuir volume after the fracturing fluid treatment.

Therefore, the relationship between the damage factor of methane and CO₂ adsorption of each group of coal samples and the fracturing fluid concentration is plotted as shown in Fig. 8. The damage factor of gel fracturing fluid to coal methane sorption capacity is significantly higher than the damage factor to CO₂ in coal as illustrated in Fig. 8 and Fig. 7b. There is no

direct correlation between the damage factor of methane adsorption and the concentration of the fracturing fluid, indicating that even at a lower concentration level, the fracturing fluid has decent damage on coal methane sorption capacity. As the concentration of fracturing fluid increases, the CO₂ adsorption damage factor starts with ~20% and increase up to ~35% and then plateaued at 35%.

Fig. 8 Variation curve of α of methane and CO₂ in coal with the increase of fracturing fluid concentration

Figs. 4 to 7 show that regardless of the raw coal or the coal sample treated with fracturing fluid, both adsorption and desorption processes show different degrees of hysteresis, that is, the sorption is not completely reversible, resulting in a hysteresis loop between the adsorption and desorption curves. In other words, in the process of pressure reduction, part of the previously adsorbed methane molecules failed to desorb and transport out. The hysteresis of coal adsorption and desorption of methane or CO₂ has been observed for a long time (Anderson et al. 1966), scholars have proposed a variety of hypotheses about the internal mechanism of adsorption and desorption hysteresis. In the early days, Bell et al. believed that the hysteresis phenomenon was due to the excessive activation energy between gas molecules and coal macromolecules in the desorption phase (Wang et al. 2016). In addition, long-term observations have identified various factors, including temperature, moisture, and coal rank, can affect the hysteresis of coal gas sorption. For the quantitative evaluation of the degree of hysteresis, there are also many methods, such as Freundlich index (Baskaran 1999), solid phase equilibrium concentration (Chen et al. 2004), or evaluation based on the slope of the adsorption-desorption curve and the difference in the area under the curve (Braida et al. 2003). In this study, the average hysteresis index (AHI) index proposed by Zhu et al. (1996) is used to

quantitatively evaluate the degree of adsorption and desorption of coal samples. The essence of this method is to integrate the percentage of the area under the desorption curve and the area under the adsorption curve. The specific calculation process is as follows:

$$AHI = \frac{A_{de} - A_{ad}}{A_{ad}} \times 100\% \quad (4)$$

$$A_{ad} = \int_0^{P_f} \frac{V_L^{ad} P}{P_L^{ad} + P} dP = V_L^{ad} \int_0^{P_f} \left(1 - \frac{P_L^{ad}}{P_L^{ad} + P}\right) dP \quad (5)$$

$$= V_L^{ad} \left[P_f - P_L^{ad} \ln\left(1 + \frac{P_f}{P_L^{ad}}\right) \right]$$

$$A_{de} = \int_0^{P_f} \frac{V_L^{de} P}{P_L^{de} + P} dP = V_L^{de} \int_0^{P_f} \left(1 - \frac{P_L^{de}}{P_L^{de} + P}\right) dP \quad (6)$$

$$= V_L^{de} \left[P_f - P_L^{de} \ln\left(1 + \frac{P_f}{P_L^{de}}\right) \right]$$

where, A_{ad} and A_{de} respectively represent the area under the isotherm adsorption line and the isotherm desorption line, P_L^{ad} and P_L^{de} respectively represent the Langmuir pressure corresponding to the isotherm adsorption and desorption process, V_L^{ad} and V_L^{de} respectively represent the Langmuir volume corresponding to the isotherm adsorption and desorption process, and P_f is the maximum equilibrium pressure value. The AHI value of 0 means that the adsorption and desorption process is reversible without hysteresis. The larger the AHI value, the more significant the hysteresis is.

Fig.9 Variation of AHI index with increasing concentration of coal samples in each group

It can be seen that the AHI value of raw coal is negative, indicating that the amount of methane desorption is greater than the actual amount of adsorption. This phenomenon is

theoretically impossible, but similar reports have appeared in previous studies (Harpalani et al. 2006; Wang et al. 2014). One possible reason of the negative value of AHI may be attributed to the nonequilibrium during the adsorption or desorption process. For methane sorption, the general trend for the sorption hysteresis increases with fluid treatment as illustrated in Fig. 9. After two high concentration fracturing fluids (0.8% and 1.2% concentration levels) treatments, the AHI index of methane desorption suddenly increased from negative values to 17.63 and 16.24. The calculation results of CO₂ AHI show that the hysteresis occurs when the CO₂ of the raw coal is desorbed, and after the raw coal is treated with fracturing fluid, the degree of hysteresis has increased to a certain extent. Compared to methane experiments, the high concentration fracturing fluid treatment did not show a sudden increase in the degree of CO₂ desorption hysteresis.

5.2 The residue distribution and functional group changes of coal samples

After the coal samples were dried, 1 g of coals are randomly selected from each group, and they were evenly placed in the sample tray for microscope observation. The results are shown in Figure 10. We observed that the surface of the raw coal particles is smooth and has less impurities (Fig. 10a). After treatment with a 0.2% concentration gel fracturing fluid, a thin coated layer of white flocculent residue was observed on the surface of the coal sample, but the overall structure of the residue is relatively loose (Fig. 10b). The coal sample treated with the 1.2% concentration fracturing fluid has extremely dense/thick surface residues, presenting a solidified colloidal film state (Fig. 10e). It can be inferred that after fracturing fluid treatment, the change of coal adsorption of methane and CO₂ gas may be caused by the adhesion of residues on the coal surface.

Fig.10 Microscope pictures of the surface of coal particles in each group (Huang et al. 2019)

Notes: a Raw coal; b Coal sample treated with 0.2% concentration fracturing fluid; c Coal sample treated with 0.4% concentration fracturing fluid; d Coal sample treated with 0.8% concentration fracturing fluid; e Coal sample treated with 1.2% concentration fracturing fluid

If a coal is reactive to the coal surface component, the greater the concentration of the fracturing fluid, the stronger the degree of chemical reaction and the more significant the functional group modifications. To observe the changes of coal surface chemical composition, we selected the highest concentration of 1.2% fracturing fluid to treat coal samples for testing. The result was shown in Fig.11. The blue and yellow spectral lines show the distribution of functional groups of the raw coal and the coal sample treated with 1.2% fracturing fluid. It can be found that after fracturing fluid treatment,

multiple peaks increase in the two wavenumber ranges of 900 – 1600, 2750 – 3000 and 3100 – 3700.

To verify whether there is a chemical reaction between the fracturing fluid and the coal surface components, the treated coal sample was immersed in distill water for 2 hours cleaning and washing. Followed by drying, the infrared green spectrum showed the distribution characteristics of functional groups of coal samples after one the infrared absorption peak decrease to some extent, especially in the wavenumber range from 3100 to 3700. After

water washing again, we observed that the height and area infrared spectrum morphology tends to recover back to the raw coal. From this data, it is confirmed that no significant chemical reaction between the fracturing fluid and coal surface functional groups during coal sample treatment. After the coal sample is treated with fracturing fluid, the change of infrared spectrum is caused by the components of gel fracturing fluid mixed into the coal structure.

Fig. 11 Infrared spectrogram of raw coal and coal samples treated with fracturing fluid

Fig.12 The chemical structure of hydroxypropyl guar

Table 1 Main functional groups contained in guar macromolecules and their attribution interval of infrared spectrum peak

Wave number	Functional group	Attribution
3624-3613	-OH	Hydroxyl
3040-3010	-CH ₃	Unsaturated stretching vibration of methyl group
2975-2915	-CH ₂ 、-CH ₃	Asymmetric stretching vibration of methyl and methylene
2875-2858	-CH ₂ 、-CH ₃	Symmetrical stretching vibration of methyl and methylene
1449-1439	-CH ₂	Methylene shear vibration

1384-1379	-CH ₃	Symmetrical bending vibration of methyl group
1379-1373	-CH ₃	Methyl shear vibration
1040	C-O-C	Alkyl ether

As described in Section 2, the main organic components of fracturing fluid include hydroxypropyl guar and organic boron. Among them, hydroxypropyl guar is a macromolecular polymer, the chemical formula of its molecular unit is shown in Figure 12, and its various functional groups and infrared spectrum peaks are shown in Table 1. Based on the measured data, the hydroxyl, methyl, methylene and alkyl ether contained in guar molecules in the residue should lead to multiple infrared spectral peaks in coal samples after treatment. With extensive and sufficient water washing, the residue on the surface of coal samples can be removed, and the surface components of coal samples will tend to recover back to raw coal.

5.3 Influencing mechanisms of fracturing fluid on sorption behavior of coals

(1) Potential chemical mechanism

The chemical modification of coal surface has been extensively studied in the literature. The surface modification of coal is usually to change the functional groups of coal by chemical agents, which can reduce the adsorption capacity of coal. It is also possible to dissolve organic matter and minerals within coal matrix through chemical reactions to enhance pore connectivity (Wang et al. 2016). These chemical modifications usually require additives with active chemical properties such as strong acid and strong oxidant (Hou et al. 2017). For this current study, the gel fracturing fluid does not contain strong oxidizing or acidic additives, thus it is difficult to trigger significant chemical surface modification of the treated coal. This has been confirmed by the infrared spectrum data as shown in Fig. 11. In other words, the chemical properties of coal surface function group are stable with HPG fracturing fluid treatment.

(2) Potential physical mechanism

From direct microscopic observations, there are different forms of fracturing fluid residue distribution on the surface of coal particles. These residues attached to the coal surface can decrease the surface area of the coal and reduce the number of available methane adsorption sites, resulting in a decrease of sorption capacity at given pressure. Physically, the fracturing fluid residues invaded into fracture and pore structure of coal may block some pores within the coal matrix, reduce the pore interconnectivity, and then reduce the coal methane or CO₂ adsorption capacity. In actual coal seam fracturing and gas drainage projects, because gas occurs in coal reservoirs before fracturing, the fracturing fluid residues can block the pores, which can result in decrease trends of desorption and diffusion.

Fig. 8 illustrates that the damage factor of fracturing fluid to methane sorption is greater than that of CO₂. According to the analysis, this may be attributed to the difference in the molecular size of methane and CO₂. The dynamic diameter of methane molecule is 0.38 nm, while that of CO₂ molecule is 0.33 nm. The fracturing fluid residue that enters the pore structure of the coal adheres to the pore wall and occupies the original pore space, resulting in the reduction of the pore diameter of part of the coal pores. Some narrow pores may be formed, and only CO₂ molecules can pass through but hinder the transport of methane molecules. This is reflected by more damage for methane compared to CO₂.

It is worth noting that the results of isothermal adsorption and desorption experiments show that the treatment of fracturing fluid will aggravate the hysteresis effect of gas desorption in coal (Fig. 9). Regarding the mechanism of this phenomenon, this article proposes two possible explanations. The first is that the residue adheres to the orifice, causing the coal to adsorb gas to swell and deform leading to a pore blocking (Figure 13).

For this phenomenon, at the low-pressure adsorption stage, a small amount of fracturing fluid residue adheres to the narrower orifice, but the orifice is not completely blocked. Due to the swelling and deformation effect of methane adsorption by coal (Wang et al. 2014), the aperture of the pore can be progressively reduced with solid matrix swelling as shown in Fig. 13. When the aperture reduces to some critical value, the gas will not be able to freely transport, and the desorption and diffusion eventually cease. This induces the notable hysteresis for the desorption process. It should be noted that in the actual process of fracturing and enhancing the permeability of the coal seam, since methane invades and adsorbs in the coal seam before the fracturing residue, the residue does not participate in the early methane adsorption stage, so it is different from the experimental design of isothermal adsorption. Therefore, the conclusion that incomplete plugging caused by adsorption expansion turns into a fully blockage has no direct guiding significance for gas drainage. But this does prove a kind of retention characteristic of fracturing fluid residue in the pores.

The second explanation is that the fracturing fluid residue can potentially invade into the pore by the high-pressure gas, causing it to be blocked, and cannot be discharged during the pressure reduction process (Fig. 13). The fracturing fluid residue is attached to the pores. For low pressure, methane can normally enter the pores and be adsorbed. At the higher pressure, the pressure in the sample cell increases, pushing the residue attached to the pore into a narrower area deep in the pore, forming a stable blockage structure. In the later desorption stage, due to the adhesion of the residue on the pore wall and the frictional resistance between the two, the residue will not be come off from the pore entry, and the gas molecules that have entered the deep part of the pore cannot be desorbed normally, resulting in

the hysteresis. It can be speculated that in the actual fracturing process, fluid pressures of up to tens of megapascals are very likely to drive fracturing fluid into the pores and fractures of the coal seam, hindering the normal desorption and flow of gas, and adversely affecting gas drainage.

Fig.13 Two mechanisms of increased desorption hysteresis of coal sample treated by fracturing fluid

From the perspective of coal seam gas drainage, to eliminate the gel-based fluid formation damage, the fracturing fluid gel breaking process should be further improved toward a fully gel breaking and flowback. After fracturing is promoted, the fracturing fluid can be fully retreated from the coal seam borehole, reducing the amount of retention in the reservoir. We can also consider to continuously improve the fracturing fluid formula, effectively control the size of fracturing fluid residue particles, change its rheological characteristics and physical interaction characteristics with coal, and prevent fracturing fluid residues from entering the coal pores, to minimize the impact of fracturing fluid on gas drainage efficiency.

6 Summary and Conclusion

- (1) The gel fracturing fluids can decrease the gas sorption capacity through physical residue coverage and pore blockage.
- (2) The chemical properties of coal surface function group did not change because no chemical reaction was observed through

FTIR measurements.

- (3) As the concentration of fracturing fluid increases, the density of residues on the coal surface increases, and the adhesion structure becomes denser. The adhesion of residues on the surface of coal walls can result in a decrease in the number of adsorption sites for gas molecules, and the blocking of pores can decrease the interconnectivity of the pore network in coal.
- (4) With gel fracture fluid invasion, the desorption hysteresis effect of methane and CO₂ in coal is intensified, and the impact on the methane desorption hysteresis is obviously greater than that on the CO₂ desorption hysteresis.

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Conflict of interest statement

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Figures

Figure 1

HPT-SDVS sorption system in the lab.

Figure 2

Microscopic coal surface fracturing fluid observations.

Figure 3

Methane sorption isotherms of IL raw coal

a

b

c

d

Figure 4

Methane ad-/desorption isotherms of coal treated by fracturing fluids with different HPG concentrations

Figure 5

CO2 ad-/desorption isotherm of raw coal

Figure 6

CO₂ ad-/desorption isotherms of IL coal treated by fracturing fluids

a. Methane adsorption and desorption

b. CO₂ adsorption and desorption

Figure 7

The ad-/desorption Langmuir volume of each group of coal samples

Figure 8

Variation curve of α of methane and CO₂ in coal with the increase of fracturing fluid concentration

Figure 9

Variation of AHI index with increasing concentration of coal samples in each group

Figure 10

Microscope pictures of the surface of coal particles in each group (Huang et al. 2019) Notes: a Raw coal; b Coal sample treated with 0.2% concentration fracturing fluid; c Coal sample treated with 0.4% concentration fracturing fluid; d Coal sample treated with 0.8% concentration fracturing fluid; e Coal sample treated with 1.2% concentration fracturing fluid

Figure 11

Infrared spectrogram of raw coal and coal samples treated with fracturing fluid

Figure 12

The chemical structure of hydroxypropyl guar

Figure 13

Two mechanisms of increased desorption hysteresis of coal sample treated by fracturing fluid