


Research Article

An Experimental Study on CO₂ Displacing CH₄ Effects of Different Rank Coals

Mingxue Li,¹ Yonghan Long,^{2,3} Lucheng Guo,² Shipan Zeng,² Jiacheng Li,² and Lei Zhang¹ 

¹School of Materials Science and Physics, China University of Mining & Technology, Xuzhou, Jiangsu 221116, China

²School of Mines, China University of Mining & Technology, Xuzhou, Jiangsu 221116, China

³CCTEG Chongqing Research Institute, Chongqing 400037, China

Correspondence should be addressed to Lei Zhang; leizhangcumt@163.com

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In order to study the effect of different rank coals on the displacement of CH₄ by CO₂ and prevent the gas-related disasters, a series of experiments were carried out. For this purpose, we selected low-rank lignite raw from Datong coalfield of Shanxi Province, medium-rank bituminous coal raw from Xutuan coalfield of Anhui Province, and high-rank anthracite raw coal from Yangquan coalfield of Shanxi Province. The results showed that (1) the shape of the displacement adsorption curve of the mixed gas and the shape of the single-dimensional adsorption curve of the pure gas are both steep at the beginning, with the increase of the pressure, the curve becomes more and more gentle. The difference is that it is lower than the single-dimensional gas adsorption curve. (2) The separation factor in the coal samples used in the experiment shows a trend of first decreasing and then increasing with the decrease of coal rank. The displacement factor has the same trend as the separation factor of each coal rank, which is Z_{ij} (anthracite) > Z_{ij} (lignite) > Z_{ij} (bituminous coal). (3) The amount of displaced CH₄ in the displacement/adsorption process has enhanced with the increase in pressure, and the trend for different coals is Q_Z (bituminous coal) > Q_Z (anthracite) > Q_Z (lignite). In addition, displacement showed the order η (lignite) > η (anthracite) > η (bituminous coal). The injection ratio of bituminous coal and anthracite decrease with the increase in pressure, while that of lignite increase first and later decreased. (4) In gas injection displacement, on the long time, the displacement effect of high coal rank is better than that of low coal rank.

1. Introduction

Coalbed methane (CBM) extraction, which is considered an efficient green technology, has attracted extensive attention in recent years [1–4]. However, Chinese coalbed methane resources are deeply buried and display poor permeability [5]. For this reason, it is difficult to increase CBM production using traditional methods. Different techniques including deep hole blasting, gas injection for enhanced coalbed methane recovery (ECBM), hydraulic fracture, and hydraulic slotting, among others, have been proposed to improve CBM production. Nevertheless, several limitations have been reported. For example, CBM wells usually display large production rates at the initial stages of the process, rapidly decreasing as pressure also decreases. Moreover, China's coal seam permeability is low. For these reasons, relevant auxiliary means are needed to assist

during CBM extraction. In this context, field test results have shown that CBM production can be improved using gas displacement methodologies. Herein, the power provided by continuous gas injection maintains a constant coal seam pressure and as a consequence, the production in coalbed methane wells can be maintained for long periods of time.

Scholars at home and abroad have done a lot of research on gas injection displacement [6–8]. The first thing of gas injection displacement we need to consider is the low permeability of coal seams in China mentioned above. Therefore, many scholars have done a lot of research on permeability. Among them, Zhang et al. [9–15] have made in-depth research on permeability changes under cyclic loading and unloading conditions especially on permeability changes of intact, fractured, and broken coal samples with different particle sizes under this condition. The influence law of effective stress on permeability under cyclic

loading condition and the change of permeability stress sensitivity under this condition are obtained. In addition, some scholars have conducted corresponding experimental research on the adsorption characteristics of coal during gas injection displacement. Clarkson et al. [16] proposed a multicomponent adsorption model for coalbed methane sorption. The model was derived from the Dubinin-Polanyi theory. Its application includes multicomponent adsorption and simulation for enhanced CBM recovery. Fitzgerald et al. [17] used the Langmuir extended equation to predict the adsorption capacity of a mixture of gases and found out that the Langmuir parameter for single components resulted in significant uncertainties. Bachu et al. [18] proposed a numerical model of gas diffusion/adsorption, which considered nonlinear adsorption in micropores, bimodal pore volume distribution, and time-varying gas pressure outside coal particles. According to Busch et al. [19], moisture greatly influences the amount of mixed gas adsorbed on coal. Katayama [20] reported that compared to N_2 , CO_2 displacement provides better performance when driving and replacing gas at the same time. Domestic scholars have investigated the adsorption and desorption of mixed gases (mainly CO_2 , CH_4 , and N_2). Tang et al. [21] conducted binary CH_4 adsorption and desorption experiments using N_2 and CO_2 and determined that coal adsorption capacity followed the order $CO_2 > CH_4 > N_2$. The disadvantage of using a weak adsorbent gas during competitive adsorption is that the strongly adsorbed gas will be more difficult to desorb. Thus, displacement of CH_4 using N_2 would be lower as compared to CO_2 . Liang et al. [22] studied the displacement of coal seam CH_4 through CO_2 injection and found out that the permeability of the coal body towards CO_2 was more than 2 orders of magnitude higher than that for CH_4 . The CO_2 stored in the coal body is related to the volume ratio of CO_2/CH_4 replacement, volume stress, and displacement pressure. The effect of CO_2/CH_4 displacement is determined by the CH_4 content in coal seam, reservoir structure, permeability, gas injection pressure, and gas injection flow rate. Zhang et al. [23] studied the influence characteristics of permeability on pore pressure during gas injection and displacement. Zhang et al. [24] conducted adsorption and desorption experiments of mixed CH_4 and CO_2 gases at different concentrations and determined that the higher the concentration of CO_2 , the more CH_4 can be replaced. Yu et al. [25] carried out CH_4 adsorption experiments on Jin Cheng and Lu An No. 2 Coal and used 8 models including Langmuir, Extended Langmuir, BET, D-R, D-A, and Toth to fit the experimental data with SPSS. These researchers found that these models displayed good CH_4 data fitting. In addition, the D-A model produced the highest fitting degree, and the critical saturated vapor pressure was calculated by empirical formula in the BET model. Yang et al. [26] also studied the displacement and adsorption of CO_2-CH_4 . Through the experiments on coal samples of different coal ranks, it was found that the higher the coal rank, the greater the adsorption capacity for CH_4 and CO_2 . The displacement capacity and displacement rate increased with the increase in pressure. However, the injection displacement ratio decreased when pressure increased. Zheng et al. [27] think coal of different coal rank has different adsorption capacity for different gases. Wang X et al. [28] carried out in the competitive adsorption the displacement effect of higher rank coal is more

obvious than that of lower rank coal. Li et al. [29] think there is an asymmetric U-shaped relationship between gas desorption and initial diffusion coefficient and coal rank. Ye et al. [30] studied adsorption law of single gas and multi gas in Xutuan coal mine.

Injection displacement involves the coupling relationship of multiple physical fields (temperature field, stress field, and seepage field) and is a complex process of adsorption, desorption, and diffusion of mixed gases. At present, most scholars have carried out significant research on adsorption and desorption in single-rank coal samples. However, there is a lack of knowledge on the effect of rank and coal characteristics on displacement. In the present research, we selected representative low-grade lignite raw from Datong coalfield in Shanxi Province, representative medium-grade bituminous raw coal from Xutuan coalfield in Anhui Province, and representative high-grade anthracite raw coal from Yangquan coalfield in Shanxi Province. A series of experiments were performed to study the displacement of adsorbed CH_4 by injecting CO_2 . We analyzed and discussed different parameters including changes in separation factor, displacement factor, displacement volume, and injection ratio, among others. The results presented herein will serve as reference to improve the theory behind displacement of coal bed methane through CO_2 injection.

2. Experimental Design for CO_2 Replacement of CH_4 Adsorbed on Coal Samples of Different Ranks

2.1. Coal Samples and Experimental Equipment. In order to study the effect of coal rank on gas adsorption, three raw coal sources with different ranks were selected. (1) Lignite was taken from No. 14-2 coal seam in Datong coalfield in Shanxi province, (2) bituminous coal was collected from No. 32 coal seam of Xutuan coalfield in Anhui province, and (3) anthracite originated from No. 15 coal seam of Yangquan coalfield in Shanxi province. Table 1 shows the results of the proximate analysis of the coal samples.

Figure 1 shows the diagram of the system used in the present research [31]. This system measures the gas adsorption capacity of coal samples by subtracting the amount of free gas in the cylinder from the total amount of injected gas. For this purpose, the volume of the sample cylinder is measured with helium (He). Later, the gas adsorption capacity is determined according to changes in cylinder pressure, which is calculated using the ideal gas equation and SRK equation.

2.2. Experimental Scheme. In this experiment, CH_4 was first injected into the cylinder until it was completely absorbed onto the coal sample. The cylinder was maintained in a water bath at constant temperature. Subsequently, CO_2 was injected into the cylinder and maintained for the same period of time as CH_4 . Finally, the exhaust gas in the cylinder was collected, and its concentration was determined using gas chromatography. The specific steps are shown in Figure 2.

TABLE 1: Proximate analysis of coal samples.

Coal rank	Water content M_{ad} (%)	Ash content A_{ad} (%)	Sulfur content S_{td} (%)	Volatile matter content V_{daf} (%)
Lignite	3.28	10.64	1.06	29.45
Bituminous coal	1.51	18.85	0.68	25.39
Anthracite	1.79	16.37	1.64	8.29

3. Experimental Results and Analysis

3.1. Pure Gas Adsorption on Coal Samples with Different Ranks. Langmuir curves and Langmuir parameters of pure gas adsorption for the three coal ranks are shown in Figure 3. Data indicated that CH_4 and CO_2 adsorption capacity of coal samples increased with the increase in pressure. In addition, at low pressure values, the adsorption capacity rapidly increased and gradually decreased with the increase in pressure.

Data in Figure 3 and Table 2 indicated a good fitting. Thus, the Langmuir equation properly described the adsorption of CO_2 and CH_4 in all coal samples. In general, we found out significant differences in CH_4 adsorption capacity of different coal ranks. According to Langmuir volume V_L , the adsorption capacity followed the order anthracite > bituminous coal > lignite, showing an increasing trend with the rise of coal rank.

3.2. Comparison between Displacement Adsorption Capacity and Pure Gas Adsorption Capacity of Different Coal Ranks. According to Figure 4, the adsorption of pure gas and mixed gas displacement/adsorption followed a similar trend. At the beginning of the process, small pressure variations caused a sudden increase in adsorption capacity. Later, as pressure increased, variations were less abrupt. However, in the three coal samples, the adsorption capacity of pure gas was greater than that of displacement/adsorption at a given pressure. Both CH_4 and CO_2 followed this pattern. In addition, at a given pressure value, the partial pressure of each component in the mixed gas was smaller than that of pure gas. The smaller the pressure, the smaller the adsorption capacity. Thus, the adsorption capacity of each component in the mixed gas was smaller than that of pure gas. It was also determined that the total amount of mixed gas adsorbed was between that of CO_2 and CH_4 as pure gases. In addition, as a result of the interaction between all the components in the system, the total amount of mixed gas adsorbed on coal was higher than that of the least adsorbed pure gas, and lower than that of the most adsorbed pure gas. Data indicated that coal displayed a high adsorption capacity for CO_2 when this gas was mixed with CH_4 . Thus, when CH_4 and CO_2 molecules are competing, it is easier for CO_2 to enter the adsorption sites in coal. Therefore, the adsorption capacity of CO_2 in replacement adsorption processes is much higher than that of CH_4 .

In the present research, CH_4 and CO_2 adsorption capacities, and the CO_2/CH_4 ratio of three coal samples of different ranks were compared. Results are displayed in Figures 5

and 6. According to our results, under the same pressure, the adsorption capacity of CO_2 on coal was much greater than that of CH_4 . There was a large difference between CO_2 and CH_4 adsorption capacity in coal. In addition, the CO_2/CH_4 ratio in different rank coal samples also showed great differences. As coal rank increased, the CO_2/CH_4 ratio displayed a “V” shape trend, where high values were observed for lignite and anthracite, and low values for bituminous coal. The CO_2/CH_4 ratio showed a linear decreasing trend with increasing pressure. The lowest CO_2/CH_4 ratio corresponded to bituminous coal, which highest value was of only 2.8. In addition, the highest CO_2/CH_4 ratio was that of anthracite with a value of 5.3, and that of lignite was 4.8. As results indicated, these two were much higher than that of bituminous coal. This is obviously related to CO_2 and CH_4 adsorption capacity of coal samples. To the best of our knowledge, the process by which CO_2 is more easily adsorbed on coal than CH_4 is not fully clear. Some scholars have hypothesized that the higher the boiling point of the gas, the stronger the adsorption capacity. The boiling point of CO_2 is about $80^\circ C$ higher than that of CH_4 ; this may explain why coal presents stronger adsorption capacity for CO_2 .

Relative differences in molecular sizes between CO_2 and CH_4 will also affect the adsorption capacity and pore permeability of coal. The molecular radius of CO_2 is 0.289 nm, while that of CH_4 is 0.310 nm. Thus, since CO_2 is smaller than CH_4 , it can reach not only macropores and micropores but also ultramicropores. In addition to the relatively small molecular diameter, the adsorption energy of CO_2 is also greater than that of methane in most pore sizes. In consequence, CO_2 diffuses into microporous coal matrix in an easier way as compared to CH_4 . The smaller molecular diameter and larger adsorption energy of CO_2 make the diffusion rate of CO_2 in coal matrix significantly higher than that of CH_4 .

The difference of CO_2 and CH_4 adsorption may also be related to the different adsorption mechanism of the two adsorbents. In other words, for CH_4 , the main mechanism involves adsorption into micropores. In the case of CO_2 , this gas is not only adsorbed into micropores but also dissolved in the structure of organic matter present in coal. Milewska et al. [32] performed different calculations using their model. These researchers concluded that, although adsorption and dissolution played an important role in the storage of these two gases, the extent of CO_2 dissolution as pure gas was similar to that of adsorption. With respect to CH_4 as pure gas, the level of dissolution was much lower than that of adsorption. Similarly, Reucroft and Sethuraman [33] suggested that the amount of dissolved CO_2 increased with pressure in the

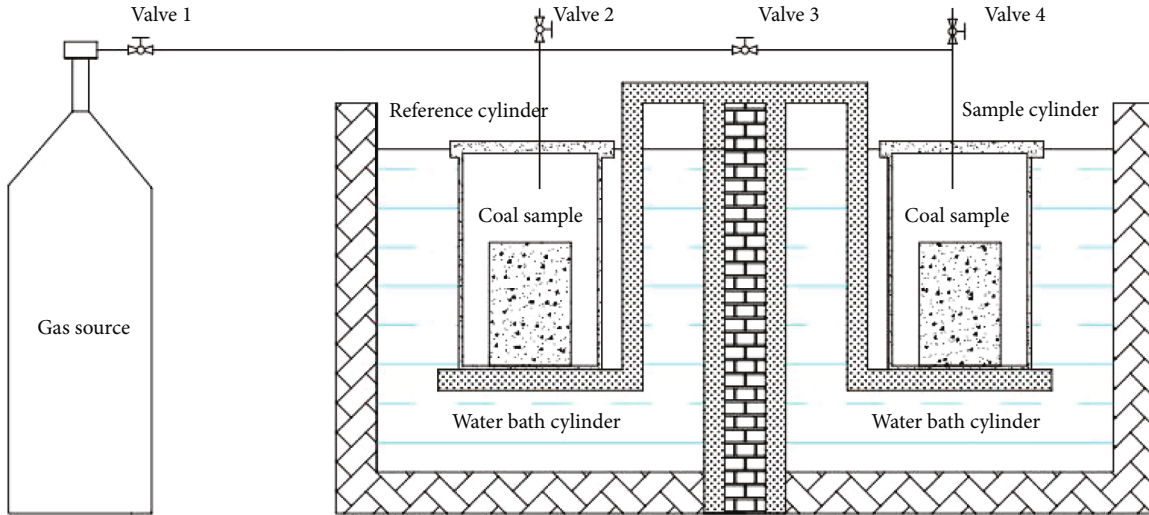


FIGURE 1: Diagram showing the system used to measure the gas adsorption capacity of coal samples.

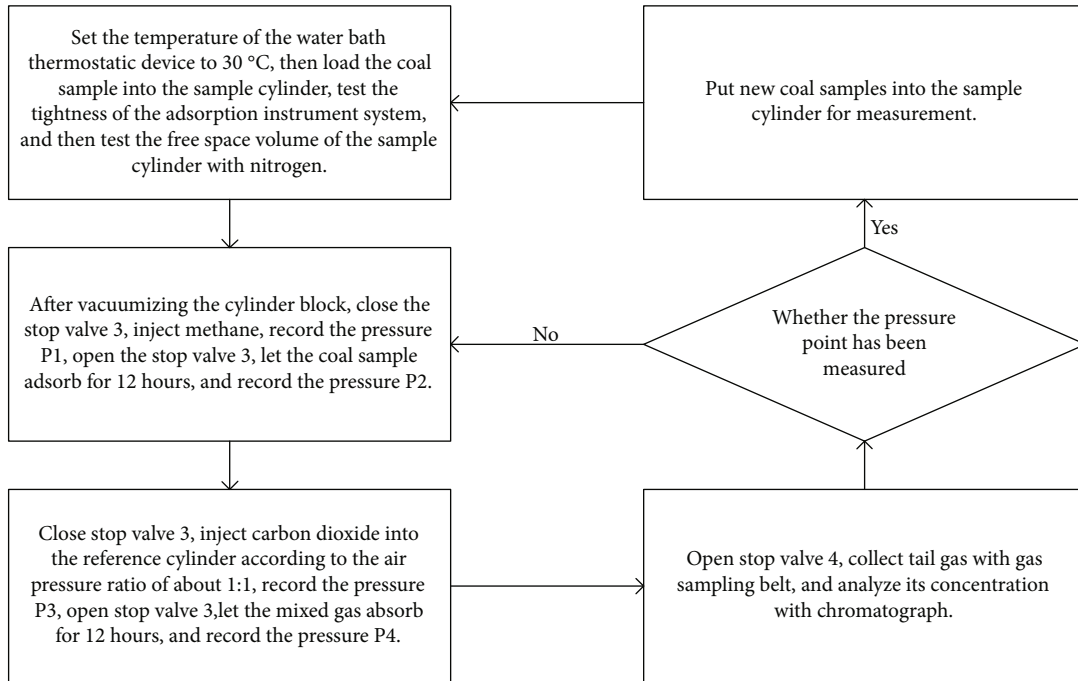


FIGURE 2: Experimental process.

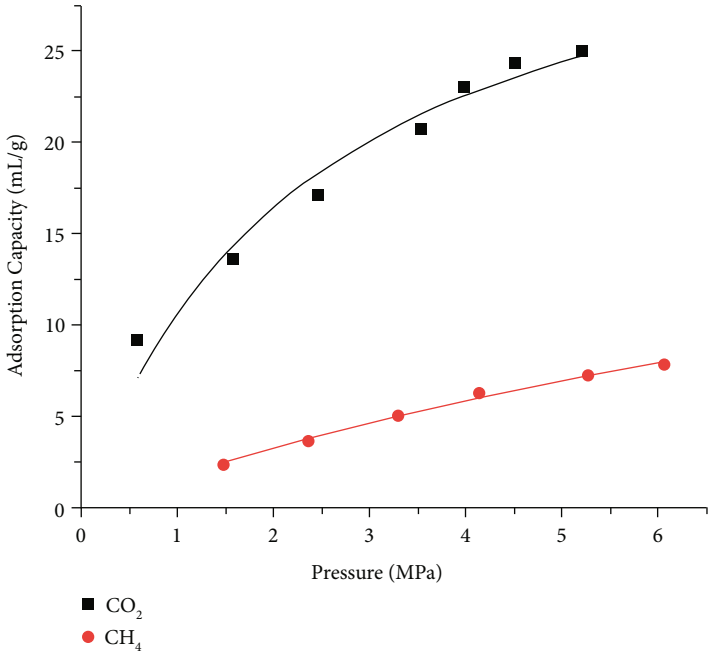
range of 5-15 atm, and half of the total CO_2 adsorbed was dissolved into coal organic matter.

Although it is generally believed that the contribution of mesopores does not affect CH_4 and CO_2 adsorption, this assumption may not be completely correct. Clarkson and Bustin [34] also proposed that when CH_4 is mainly adsorbed on the surface of micropores, CO_2 can be adsorbed not only by micropores but also by some mesopores. This may be one of the reasons of the higher CO_2 adsorption as compared to CH_4 .

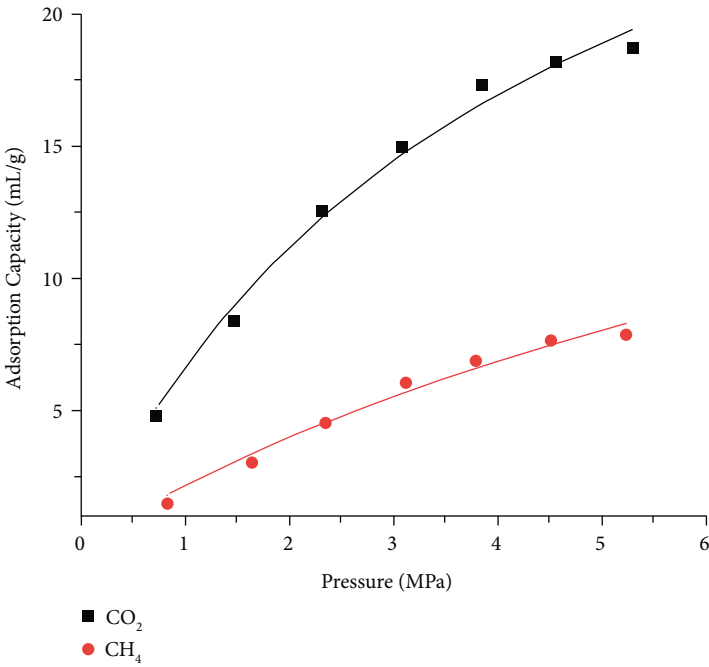
3.3. Separation Factor and Displacement Factor of Different Rank Coal Samples. The separation factor is used to characterize the adsorbability of adsorbents in mixed systems [35].

In the present investigation, adsorbability was used to indicate the degree of CO_2 and CH_4 adsorption on coal. When the ratio of adsorbed state to free state of the two gases (CO_2/CH_4) was greater than 1, the adsorption of CO_2 on coal was stronger than that of CH_4 . On the other hand, if the result was less than 1, the adsorption of coal to CO_2 was weaker than that of CH_4 . Combining the Langmuir equation, the separation factor between the two gases can be expressed as:

$$F_{ij} = \frac{a_i/a_j}{b_i/b_j} = \frac{Q_i/Q_j}{b_i/b_j} = \frac{V_{Li}/P_{Li}}{V_{Lj}/P_{Lj}}. \quad (1)$$



(a) Anthracite



(b) Bituminous coal

FIGURE 3: Continued.

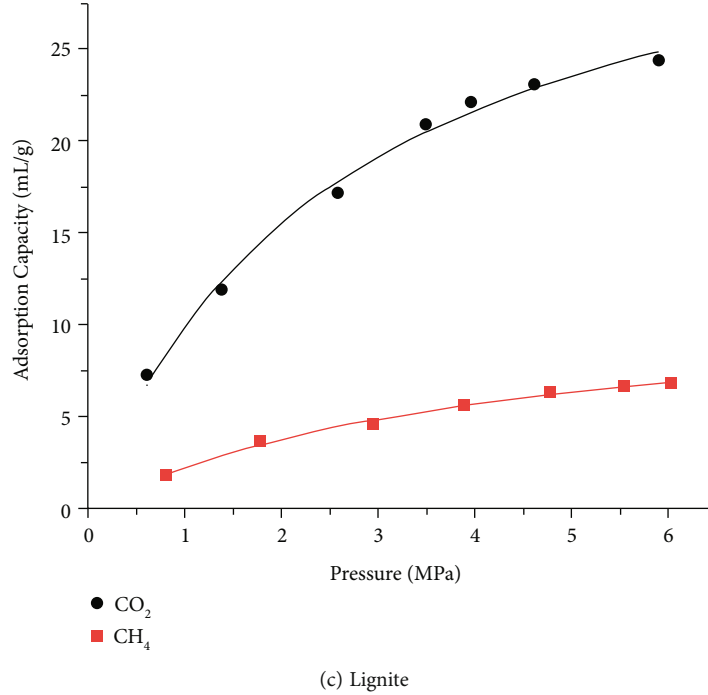


FIGURE 3: Langmuir curves of three coal samples.

TABLE 2: Langmuir parameters of different rank coal samples.

Coal rank	Gas path	V_L (cm ³ /g)	P_L (MPa)	Fitting degree R^2
Anthracite	CO ₂ adsorption	35.97	2.38	0.956
	CH ₄ adsorption	27.03	14.43	0.995
Bituminous coal	CO ₂ adsorption	35.36	4.36	0.988
	CH ₄ adsorption	25.28	10.22	0.985
Lignite	CO ₂ adsorption	35.84	2.61	0.991
	CH ₄ adsorption	11.65	4.21	0.994

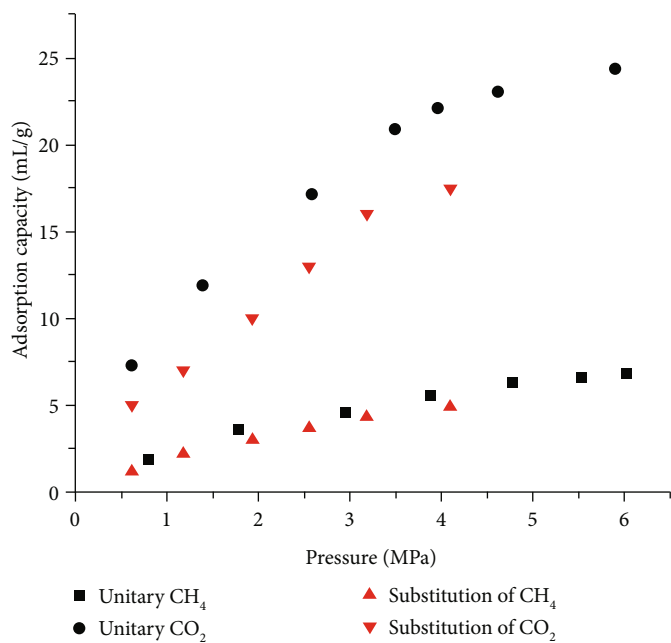
In the formula, a_i represents the volume fraction of adsorbed CO₂ in mixed adsorption; a_j indicates the volume fraction of adsorbed CH₄ in mixed adsorption; b_i is the volume fraction of free CO₂ in mixed adsorption; b_j is the volume fraction of free CH₄ in mixed adsorption; and F_{ij} is the separation factor of CO₂ to CH₄.

According to Equation (1), the separation factor derived from the Langmuir equation is only related to Langmuir pressure and Langmuir volume. The separation factors of different coal ranks are shown in Table 3.

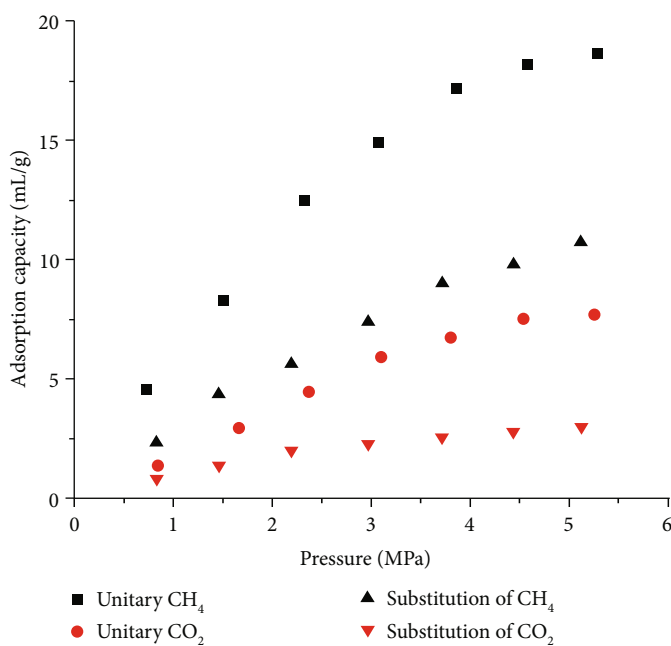
According to our data, at the initial stage, the separation factor displayed a decreasing trend with the decrease in coal rank; later, the separation factor increased. This demonstrated that the adsorption of CO₂ on anthracite was stronger than that of CH₄. Thus, the strongest and weakest CO₂ adsorption corresponded to anthracite and bituminous coal, respectively. However, separation factors of the three coal ranks were greater than 1. Adsorption results in mixed systems showed that CO₂ adsorption on coal samples was stronger than that of CH₄. However, the change in equilibrium

pressure will also affect the size of the separation factor. Figure 7 presents the separation factor of each coal sample under different equilibrium pressure values. This figure shows that, as equilibrium pressure increases, the separation factor in displacement adsorption also increases. Although the separation factor is not a fixed value, there is still a certain gap between the measured separation factor and the separation factor derived from the Langmuir equation. Especially when the pressure is low, the gap is large, and when the pressure is high, they are relatively close.

The displacement factor is used to represent the ability of one gas to replace another gas during mixed adsorption and shows the ability of the two gases to compete for the adsorption sites. Herein, we determined the ability of CO₂ to replace CH₄ in the coal samples. Because this displacement ability is also affected by the partial pressure of the gas, the extent of the adsorption in the mixed adsorption system is affected by mutual interference of the adsorption strength and the partial pressure of the gas. The separation factor is only considered in the calculation of the adsorption



(a) Lignite



(b) Bituminous coal

FIGURE 4: Continued.

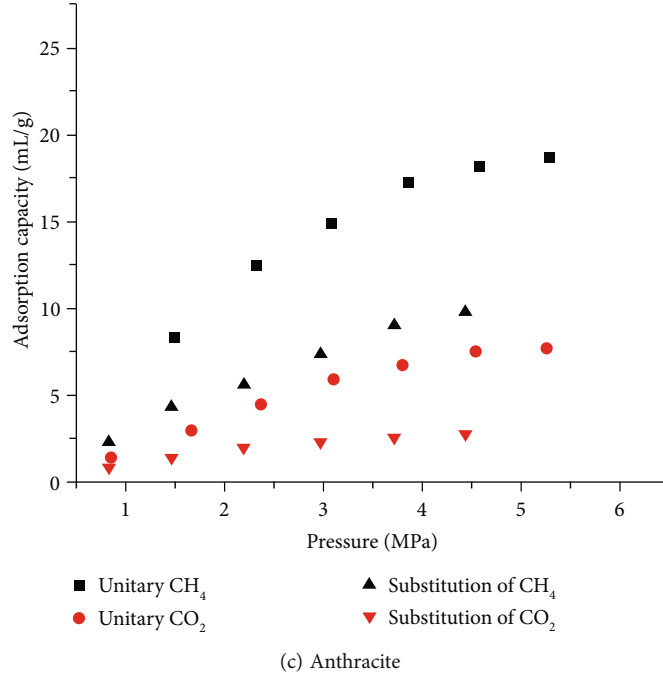


FIGURE 4: Adsorption capacity of lignite, bituminous coal, and anthracite.

strength of the coal body to CO₂ and CH₄, and there is no effect of the partial pressure of the gas component. By comparing the ratio of CO₂/CH₄ adsorption at equilibrium with that of pure gas adsorption at the same CO₂ partial pressure and CH₄ displacement/adsorption, and in combination with the Langmuir equation and the extended Langmuir equation, the displacement factor Z_{ij} can be expressed as shown in Equation (2) [36]:

$$Z_{ij} = \frac{Q_i/Q_j}{Q_{p_i}^i/Q_{p_j}^j} = \frac{P_i/P_{L_i} + 1}{P_j/P_{L_j} + 1}. \quad (2)$$

The results are shown in Figure 8, and they indicate that the replacement factors of each coal rank are all greater than 1. Thus, CO₂ was able to replace CH₄ from the coal samples. It was also found that, as pressure increases, the replacement factor also increases. This means that the higher the pressure, the easier for CO₂ to replace CH₄ from coal samples. In general, the displacement factor of anthracite was larger than that of lignite and bituminous coal, which is the same as the trend of separation factor of each coal rank. When the coal sample adsorbs the mixed gases, one component affects the other and interacts with the partial pressure during adsorption. However, since the ratio of CO₂ and CH₄ is 1 : 1, the influence of partial pressure is not obvious. Thus, the displacement factor and separation factor of each coal rank sample showed high consistency.

3.4. Displacement and Injection Ratio of Different Rank Coal Samples. In order to analyze the replacement effect of CO₂ on CH₄, in this section, we evaluated the replaced amount and injection ratio. The difference between the amount of

pure adsorbed gas and displacement of CH₄ is the displaced amount Q_z of CH₄:

$$Q_z = Q_{\text{pure}}(\text{CH}_4) - Q_{\text{displaced}}(\text{CH}_4). \quad (3)$$

The injection ratio is the ratio of displacement to injected CO₂:

$$\eta = \frac{Q_z}{n(\text{CO}_2)}. \quad (4)$$

The displacement and injection ratio of different coal ranks were calculated using pure gas adsorption and displacement of CH₄. Data are shown in Figure 9.

Data in Figure 9 indicate that the amount of replaced CH₄ in the displacement process increased with the increase in pressure. In addition, an inverted “V”-shaped trend was observed as coal rank increased. Q_z values followed the order Q_z (bituminous coal) > Q_z (anthracite) > Q_z (lignite). Moreover, at low pressure values, the amounts of gas replaced on the three coals of different ranks were similar. However, as adsorption pressure increased, the amount of replaced gas on bituminous coal increased significantly faster as compared to anthracite and lignite. It was also determined that as coal rank increased, the injection ratio presented a “V”-shaped trend, which was the opposite of the replaced amount. Injection ratio followed the order η (lignite) > η (anthracite) > η (bituminous coal). Furthermore, the injection ratio of bituminous coal and anthracite increased with the increase in pressure. On the contrary, in lignite, injection ratio first increased and later decreased.

According to the results presented in Section 3.2, the main difference in CH₄ and CO₂ adsorption capacity of coal

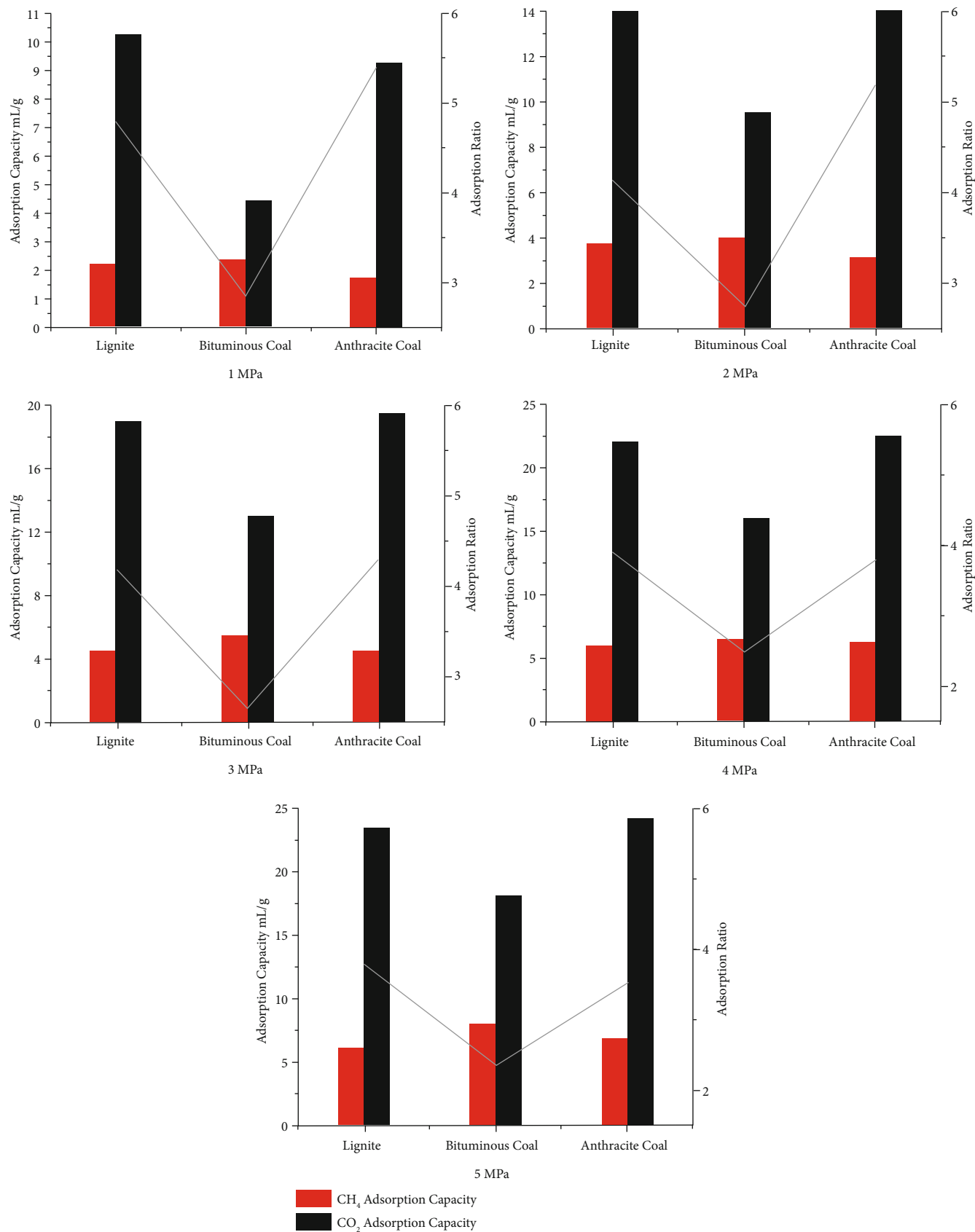


FIGURE 5: CO₂ and CH₄ adsorption capacity of different rank coal samples.

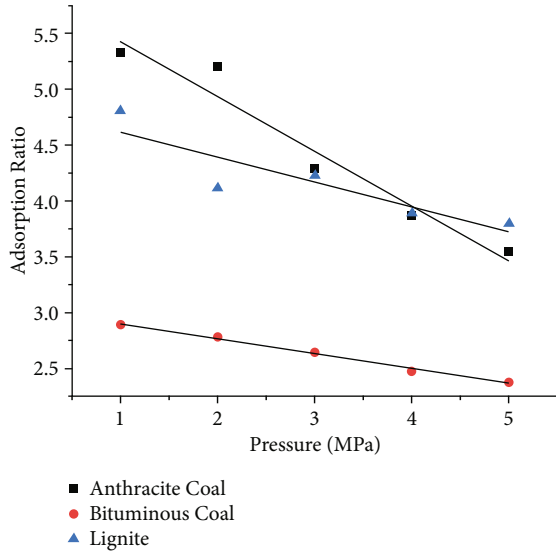


FIGURE 6: Effect of pressure on CO_2/CH_4 adsorption ratio of different rank coal samples.

TABLE 3: Separation factors of different coal ranks according to the Langmuir equation.

Coal rank	Anthracite	Bituminous coal	Lignite
Separation factor F_{ij}	8.06	3.27	4.96

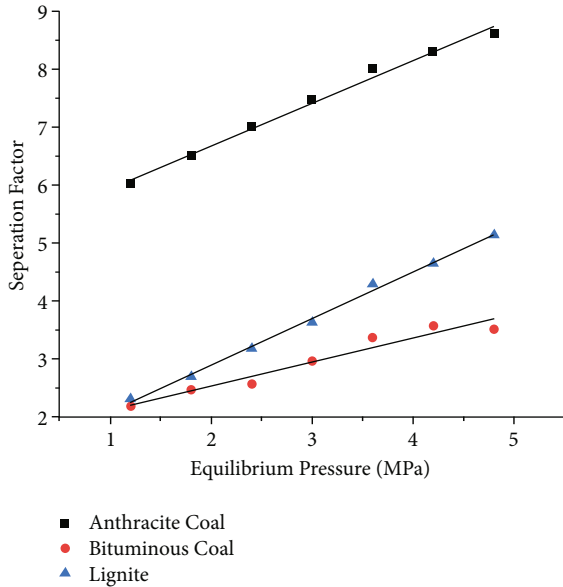


FIGURE 7: Separation coefficients of different rank coal samples.

was related to the different adsorption mechanisms. In the case of CH_4 , the main mechanism involved adsorption into micropores. On the other hand, CO_2 was adsorbed into coal micropores and dissolved in coal organic matter. In the case of competitive adsorption, only part of the CO_2 competed with CH_4 . Lignite displays high organic matter content; thus, more CO_2 can be dissolved and in consequence, less CO_2

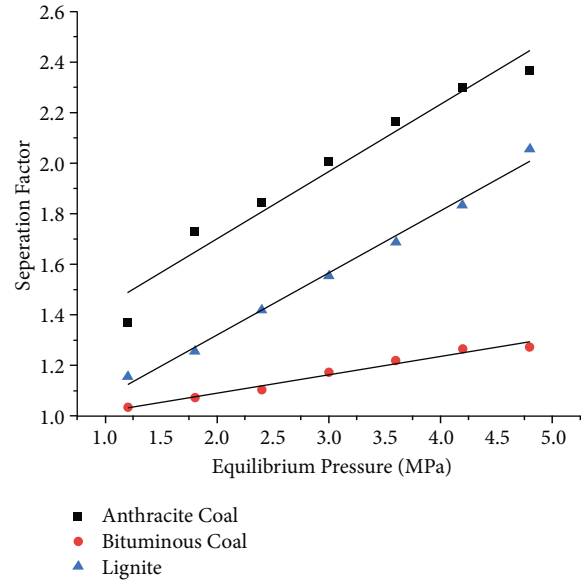


FIGURE 8: Displacement coefficient of different rank coal samples.

participates in the competitive adsorption. On the other hand, lignite showed high CH_4 adsorption capacity. Herein, low amounts of CH_4 were replaced. Moreover, low organic matter content is found in bituminous coal and anthracite. For this reason, less CO_2 is dissolved, and more CO_2 participates in the competitive adsorption. In this case, less CH_4 is adsorbed and more CH_4 is replaced. According to the injection ratio results, in order to replace a given amount of CH_4 in lignite, the amount of CO_2 needed is several times that of bituminous coal and anthracite.

3.5. The Displacement Effect of Different Coal Ranks Samples. Taking into account different indicators including displacement amount and displacement factor, data showed that the lowest separation factor and displacement factor corresponded to bituminous coal [37]. In addition, this type of coal showed the highest displaced amount. Because the displacement factor represents the ability of CO_2 to replace CH_4 from the coal sample, the separation factor is related to the adsorption of the two gases by the coal. From the point of view of molecular simulation, as the degree of metamorphism increased, the content of hydroxyl and oxygen-containing functional groups gradually decreased, and the content of hydroxyl in low-rank coal was significantly higher than that in medium- and high-rank coals. Moreover, the content of aromatic hydrocarbons increased gradually, the degree of condensation increased, and the side chain decreased. Thus, the greater the coal rank, the higher the symmetry of its molecular structure. When adsorption reaches stability, the CO_2 and CH_4 molecules adsorbed by lignite molecules are located above the benzene ring. In addition, CO_2 and CH_4 molecules adsorbed by bituminous coal molecules are located near the benzene ring and hydroxyl group, and the CO_2 and CH_4 molecules adsorbed by anthracite molecules are located near the benzene ring. The distance between CH_4 molecules and bituminous coal molecules is much larger than that of anthracite and lignite,

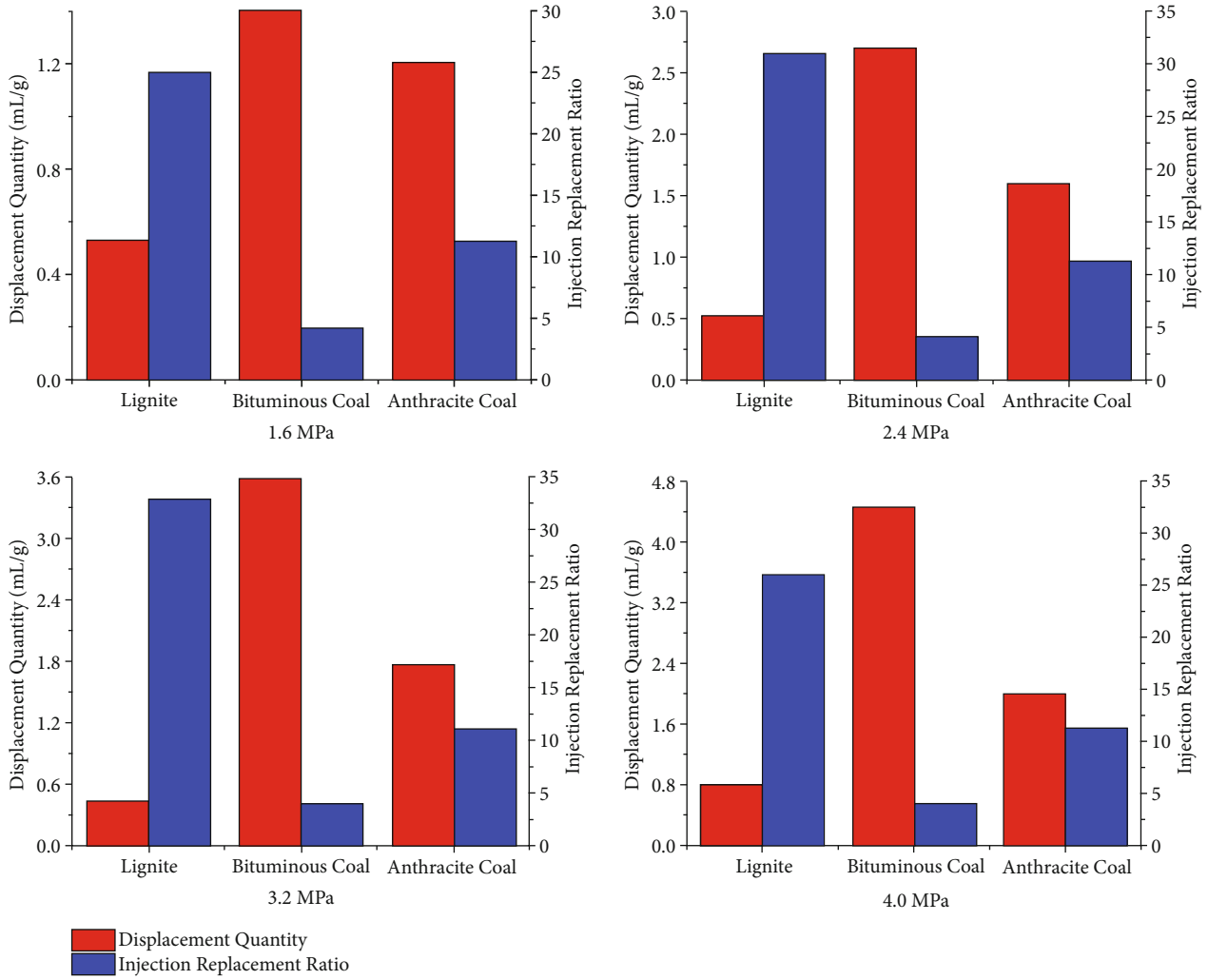


FIGURE 9: Displacement in lignite, bituminous coal, and anthracite.

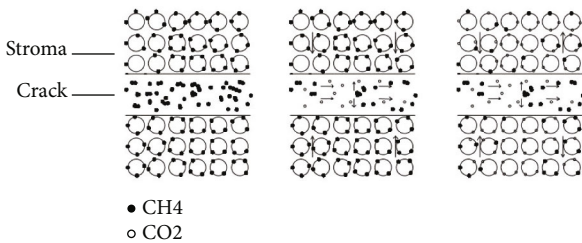


FIGURE 10: Replacement process of ECBM.

so is the case for CO₂ molecules. Thus, the lowest replacement factor was observed in bituminous coal, and its ability to replace CH₄ was weaker than that of CO₂. However, although bituminous coal showed a weak replacement capacity, a high total adsorption capacity was observed. Thus, adsorption of CO₂ and CH₄ presented elevated values. Even if the replacement capacity of this type of coal was lower than that of lignite, the overall replacement capacity was still relatively large. It was also observed that the levels of injection ratios in coal samples of different coal ranks

were consistent with changes in the separation factor and replacement factor. That is, they are all high for anthracite and lignite, but low for bituminous coal. With respect to replacement efficiency, similar injection ratios were determined in the two types of coal pairs. Also, a significant correlation was observed since the stronger the CO₂ adsorption on the coal sample, the more CO₂ was required to replace the same amount of CH₄.

CO₂ gas flooding is essentially a process of displacement and adsorption where CO₂ is injected and CH₄ is displaced from the coal structure. As a porous medium with strong adsorption capacity, coal contains a large number of pores in its matrix, and a clear system forming an orthogonal fracture network is generated during the coalization process (Figure 10). Gas flooding converts the gas in the matrix from the adsorbed state to the free state through displacement and desorption. Later, desorbed gas enters the orthogonal fracture network of the micropores through diffusion and finally leaves the coal body. This process can be roughly divided into two stages. In the first stage, the displaced CH₄ is mainly in the free state, which lasts for a short time. In the second

stage, the desorbed gas is the main gas to be displaced, and the desorption time determines the displacement. This step takes longer than the first stage. In the second stage, the displacement effect plays a leading role. According to this analysis, the CO₂ adsorbed in the micropores participates in the displacement effect during gas injection flooding, instead of the CO₂ dissolved in the organic matter. Therefore, a considerable amount of CO₂ is not replaced in the flooding process, which partly depends on the organic matter content of the coal sample. The replacement capacity of lignite is stronger than that of bituminous coal. When it can be fully replaced, the replaced amount is higher. However, because of its low adsorption capacity, the total replaced amount of CH₄ is relatively small. In addition, since lignite displays high organic matter content, more CO₂ can be dissolved, and less CO₂ actually participates in the replacement effect. This is also one of the reasons for the high replacement factor and injection ratio in lignite. When the same amount of CO₂ is injected, the CO₂ involved in the displacement effect in lignite is lower than that in bituminous coal and anthracite. The bituminous coal adsorbs more CH₄ and can continue to replace CH₄. On the long-term, the displacement and replacement effect of medium and high coal rank is better than that of low coal rank.

4. Conclusions

- (1) In our experiments, it was found that as coal rank decreased, separation factor first decreased and later increased. Nevertheless, separation factor for the three coal ranks were higher than 1. Results also indicated that coal bodies presented a better adsorption capacity for CO₂ as compared with CH₄. Herein, the replacement factor in each coal sample displayed the same trend as the separation factor. Thus, the order was Z_{ij} (anthracite) > Z_{ij} (lignite) > Z_{ij} (bituminous coal). Also, the replacement factors of each coal rank were higher than 1, and they increased with the increase in pressure. This indicated that, as pressure increased, it was easier for CO₂ to replace CH₄ from the coal sample
- (2) The amount of displaced CH₄ during displacement/adsorption increased with the increase in pressure. Q_z of different coal rank samples followed the order Q_z (bituminous coal) > Q_z (anthracite) > Q_z (lignite). With respect to injection ratio, decreasing order was η (lignite) > η (anthracite) > η (bituminous coal), where the injection ratio of bituminous coal and anthracite increased as pressured values augmented. In the case of lignite, injection ratio first increased and subsequently decreased
- (3) In the gas injection flooding process, CO₂ adsorbed in the micropores participated in the displacement effect, instead of the CO₂ dissolved in the organic matter. Therefore, a considerable amount of CO₂ did not contribute to CH₄ replacement. On the long term, the displacement and replacement effect of

medium and high coal rank is better than that of low coal rank

Data Availability

All data included in this study are available upon request by contact with the corresponding author.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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