



## Component fractionation of temporal evolution in adsorption–desorption for binary gas mixtures on coals from Haishiwan Coal Mine

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### ABSTRACT

Adsorption–desorption experiments on CO<sub>2</sub>–CH<sub>4</sub> gas mixtures with varying compositions have been conducted to study the fractionation characteristics of CO<sub>2</sub>–CH<sub>4</sub> on Haishiwan coal samples. These were carried out at constant temperature but different equilibrium pressure conditions. Based on these experimental results, the temporal evolution of component fractionation in the field was investigated. The results show that the CO<sub>2</sub> concentration in the adsorbed phase is always greater than that in the original gas mixture during the desorption process, while CH<sub>4</sub> shows the opposite characteristics. This has confirmed that CO<sub>2</sub>, with a greater adsorption ability has a predominant position in the competition with CH<sub>4</sub> under different pressures. Where gas drainage is employed, the ratio of CO<sub>2</sub> to CH<sub>4</sub> varies with time and space in floor roadways used for gas drainage, and in the ventilation air in Nos.1 and 2 coal seams, which is consistent with laboratory results.

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### 1. Introduction

Displacement of CH<sub>4</sub> by CO<sub>2</sub> injection in coal seams is an effective method, not only for sequestration of greenhouse gases, but also for enhancing coalbed methane production. This technology has been employed in a number of countries [1–4]. The adsorption–desorption characteristics of gas mixtures on coals vary with different components [5]. Yu and Tang researched the isothermal adsorption of a CO<sub>2</sub>–CH<sub>4</sub> gas mixture on coals of different rank under low pressure and adsorption model fitting; Bush and Majewska, in their adsorption experiments, showed that CO<sub>2</sub> is more likely to be adsorbed preferentially under high pressures, whereas CH<sub>4</sub> is readily adsorbed under low pressures on certain coals; Cui et al. believed that the pore structure of the coal and the molecular dynamics of the gas play important roles in the adsorption and diffusion characteristics of different gases [6–10]. Many researchers consider that competition for adsorption sites is the main feature of multi-gas adsorption in coal. However, due to the influence of coal rank, moisture in the coal samples, adsorption equilibrium conditions and other factors, the multi-component adsorption process is not consistent and often demonstrates opposite characteristics [11,12].

This paper is based on the Yaojie coalfield which experiences both coal and CO<sub>2</sub> outbursts [13]. In the laboratory, we investigated

the fractionation characteristics of adsorption–desorption for a binary gas mixture with different components on Haishiwan coal samples; in the field, we obtained the temporal evolution of component fractionation on a larger scale by the drainage of a gas mixture, which provides a basis for CO<sub>2</sub>–CH<sub>4</sub> extraction, and injection of CO<sub>2</sub> to displace CH<sub>4</sub>.

### 2. Sampling and methodology

Samples were obtained from Haishiwan Coal Mine of the Gansu Yaojie coal field, the details of which are shown in Table 1.

In the No.2 coal seam, the gas mixture is mainly CO<sub>2</sub> and CH<sub>4</sub>. The gas component of the coal seam is related to the point of injection of CO<sub>2</sub>, so adsorption experiments were carried out on four gas mixtures with different volume fractions. The ratios of CO<sub>2</sub> to CH<sub>4</sub> were 9:1, 2:1, 1:1 and 3:7. The specific test methods used were as follows:

- (1) Samples were taken from 6223 working face and prepared by crushing the coal to a particle size range of 0.2–0.25 mm.
- (2) A quantity of the 0.2–0.25 mm diameter dry coal sample was loaded into the coal sample canister which was then sealed and placed in a water bath at a constant temperature of 60 °C, and then degassed for 6–8 h.
- (3) After vacuum degassing, the coal sample canister, with valve closed, was then placed in a water bath at a constant temperature of 30 °C. A burette containing a volume of

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**Table 1**

Compositional analysis of Haishiwan coal samples (%).

Proximate analysis				Maceral analysis				
M <sub>ad</sub>	V <sub>daf</sub>	A <sub>d</sub>	FC <sub>d</sub>	Vitrinite	Inertinite	Exinite	Mineral	R <sub>o,max</sub>
1.01	30.10	3.39	66.85	48.68	47.35	2.85	1.14	0.93

experimental gas was then connected to the coal sample canister. The valve was then opened to allow the coal sample to inhale gas from the burette over a period of more than 8 h. The volume of gas inhaled, room temperature and atmospheric pressure were recorded.

- (4) Experimental gas was introduced into the coal sample canister at a pressure of 6 MPa over a period of 6 h in a constant temperature bath at 30 °C. The adsorption equilibrium pressure was recorded. The valve was then opened, allowing a small volume of gas (not greater than 100 mL) to enter the burette. The valve was then closed and a sampling bag used to remove the gas from the burette. The sampling bag was then connected to a gas chromatograph to determine the gas component.
- (5) More gas from the coal sample canister was introduced into the burette. When the gas pressure reduced to a pre-determined level, the valve was turned off and the desorption volume, room temperature and atmospheric pressure were recorded. When equilibrium was achieved, after 6–8 h, the second point to the sixth point was measured according to the above method. After finishing the sixth point, the valve was opened to measure the gas component after full desorption over a period of more than 8 h. The desorption capacities, room temperature and atmospheric pressure were then recorded.

During adsorption of a gas mixture on coal, the different adsorption properties of the gases result in the ratio of CO<sub>2</sub> to CH<sub>4</sub> to be different from the original gas mixture, which results in a change in free phase gas concentration in the coal sample canister. The gas component concentration of the adsorption phase was calculated using the following equation:

$$V_{\text{adsn}} = \sum_{i=1}^n V_i - c_n \times V_{\text{yl}} \quad (1)$$

where  $V_{\text{adsn}}$  is the quantity of CO<sub>2</sub> and CH<sub>4</sub> adsorbed;  $\sum_{i=1}^n V_i$  the cumulative release volume of balance point  $i$ ;  $V_{\text{yl}}$  the free volume of the coal sample at the balance point;  $c_n$  the concentration of CO<sub>2</sub> and CH<sub>4</sub> of free phase, obtained through experiment.

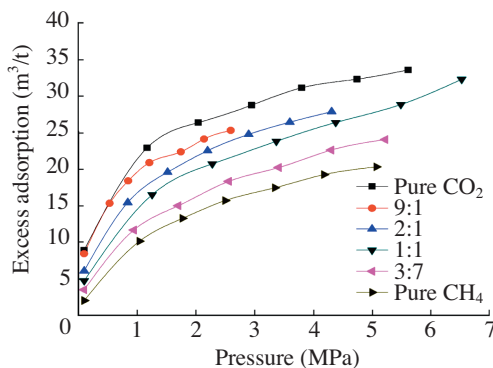
### 3. Results and discussion

#### 3.1. Component fractionation of adsorption for gas mixture on coals

Under the 30 °C condition, sorption tests with pure CO<sub>2</sub> and methane-carbon dioxide mixtures were performed on coals, as shown in Fig. 1. The adsorption isotherms of the gas mixture are in accord with I isotherm, which is consistent with the adsorption isotherm of pure CO<sub>2</sub>. The sorption capacities of CO<sub>2</sub> and CH<sub>4</sub> on coals with increasing CO<sub>2</sub> concentrations in the mixed gas have a positive correlation with CO<sub>2</sub> concentration in the gas mixture.

According to sorption tests using CO<sub>2</sub>–CH<sub>4</sub> mixtures on coals from Haishiwan Coal Mine, the adsorption isotherms of CO<sub>2</sub> and CH<sub>4</sub>, are plotted separately, as shown in Fig. 2.

As can be seen from Fig. 2: (1) The gradient of the isothermal adsorption curve of CH<sub>4</sub> in the gas mixture does not increase constantly with increasing pressure, the excess adsorption reduces



**Fig. 1.** Isothermal adsorption curves of CO<sub>2</sub>–CH<sub>4</sub> mixture on Haishiwan coal samples.

first, and then increases for the sorption of a gas mixture with different components on coals. It is significant that the ratios of CO<sub>2</sub> to CH<sub>4</sub> are 9:1, 1:1. Yu also found a similar phenomenon [6]. (2) The gradient of the isothermal adsorption curve for CO<sub>2</sub> increases with increasing pressure and the adsorption isotherms of a gas mixture with a ratio of CH<sub>4</sub> to CO<sub>2</sub> being 1:1 is in accord with IV isotherm. (3) The Langmuir equation is not suitable for describing the sorption isotherm of CH<sub>4</sub> and CO<sub>2</sub> in gas mixtures [14].

Selectivity of adsorption for a CO<sub>2</sub>–CH<sub>4</sub> mixture on coal is related to the adsorption characteristics of coal, the pore structure of the coal itself and molecular characteristics of the gas. The theory and experimental observations confirm that diffusion of CO<sub>2</sub> is faster than CH<sub>4</sub> in dry coal by about 1–2 orders of magnitude [15]. The CO<sub>2</sub> molecule kinetic diameter is 0.33, and 0.38 nm for CH<sub>4</sub>, therefore CO<sub>2</sub> can enter the smaller pores of the coal samples [10].

#### 3.2. Component fractionation of isothermal desorption for a binary gas mixture of CO<sub>2</sub>–CH<sub>4</sub>

After obtaining the adsorption capacities of CO<sub>2</sub> and CH<sub>4</sub> at each balance point, it is easy to obtain the individual gas concentration in the adsorbed phase, as shown in Fig. 3.

As can be seen from Fig. 3: (1) In the adsorption phase, the concentration of CO<sub>2</sub> is always greater than that in the original gas mixture, whereas CH<sub>4</sub> shows the opposite characteristics. This illustrates that CO<sub>2</sub> is of greater adsorption ability and is preferentially adsorbed, resulting in a relative increase in CH<sub>4</sub> concentration in the free gas phase. (2) With different combinations of gas mixture and equilibrium pressure, the CO<sub>2</sub> concentration in the adsorbed phase shows a different relationship with a gradual decrease in equilibrium pressure; when the ratio of CO<sub>2</sub> to CH<sub>4</sub> is greater than 1, the CO<sub>2</sub> concentration in the adsorbed phase remains unchanged, but if the ratio of CO<sub>2</sub> to CH<sub>4</sub> is 2:1, the CO<sub>2</sub> concentration increases markedly at 6.5 MPa equilibrium pressure, which is relevant for the interaction between coal and CO<sub>2</sub>. The adsorption space is enlarged due to softening of the coal body structure, which causes the CO<sub>2</sub> concentration in the adsorbed phase to increase [16]. When the ratio of CO<sub>2</sub> to CH<sub>4</sub> is 3:7, the CO<sub>2</sub> concentration in the adsorbed phase reduces continuously. We can postulate that when CO<sub>2</sub> adsorption capacity reaches saturation, the CH<sub>4</sub> adsorption capacity of coal will gradually increase. (3) In the desorption process, the CO<sub>2</sub> concentration in the free phase is less than that of the original gas mixture with a gradual reduction of equilibrium pressure, whereas CH<sub>4</sub> shows the opposite characteristic. This demonstrates that CO<sub>2</sub> desorbs prior to CH<sub>4</sub>. According to the desorption behaviour of gas mixtures on Haishiwan coals, separation of phase compositions of CO<sub>2</sub> and CH<sub>4</sub>

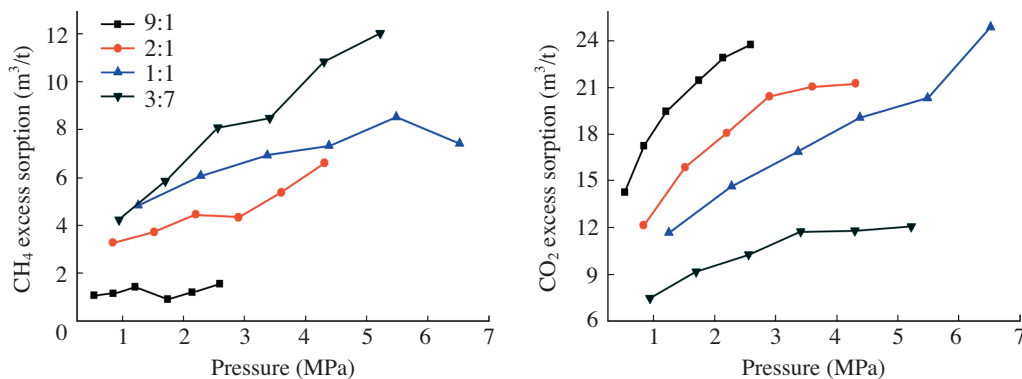


Fig. 2. Isothermal adsorption curves of CH<sub>4</sub> gas and CO<sub>2</sub> gas in the mixed gas.

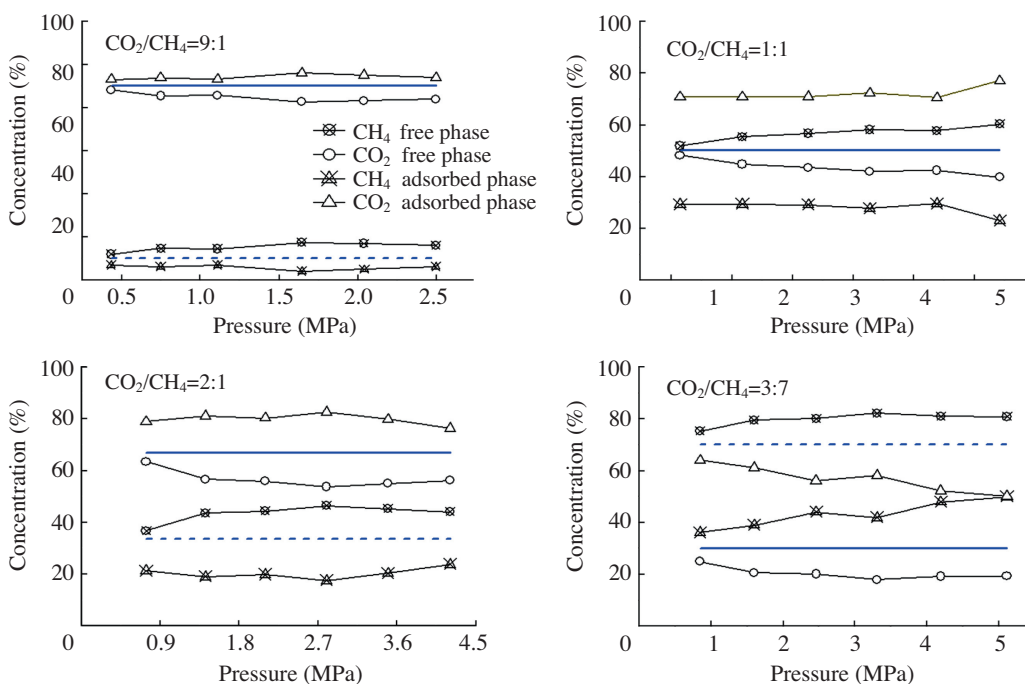


Fig. 3. Change trends of gaseous composition during binary gas sorption.

with different gas proportions in the adsorbed and free phases were demonstrated, as shown in Fig. 4.

The shape of the curve for separation of phase components is similar to an inclined spindle, as reported in the literature [17]. For the same coal sample, fixed structure and effective adsorption space, the pore width introduced for CO<sub>2</sub> and CH<sub>4</sub> is determined. In gas mixtures with different proportions, the component separation image of a binary gas mixture is relatively fixed, ignoring the interaction of CO<sub>2</sub> and CH<sub>4</sub>. On the whole, during the process of desorption, along with the decreasing concentration of CO<sub>2</sub> or CH<sub>4</sub> in the gas phase, the adsorbed phase concentration of the corresponding gas will reduce. In the CO<sub>2</sub>–CH<sub>4</sub> binary gas system, CH<sub>4</sub> competes for coal surface adsorption sites with CO<sub>2</sub>. When the CH<sub>4</sub> is at a higher concentration in the free phase, the concentration of CH<sub>4</sub> in the adsorbed phase will be drastically reduced as long as this concentration in the free phase is slightly reduced. This also explains the fact that CO<sub>2</sub> is the strong adsorbate and CH<sub>4</sub> the weak adsorbate in the CO<sub>2</sub>–CH<sub>4</sub> binary gas system. In the desorption process, CH<sub>4</sub> is desorbed preferentially, the desorption rate

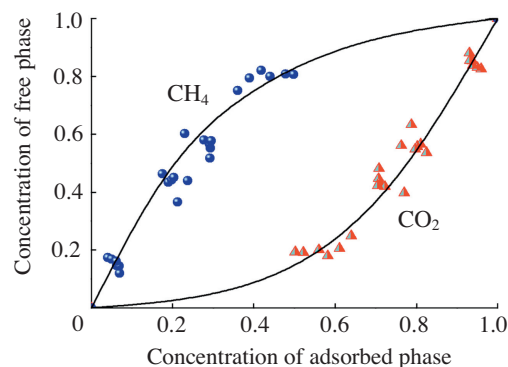


Fig. 4. Separation of phase composition of binary gas desorbed on dry coal at 30 °C.

decreases from fast to slow, while for CO<sub>2</sub> the desorption speed increases from slow to fast.

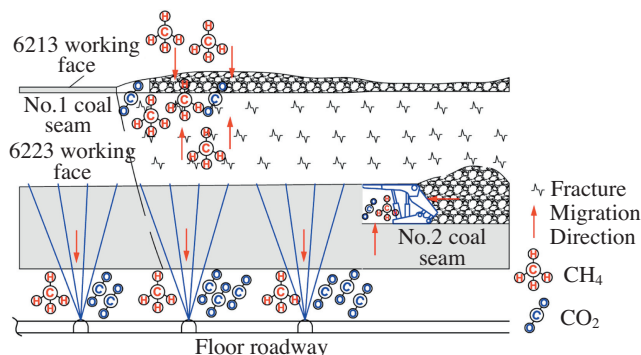


Fig. 5. Fractionation effect of  $\text{CO}_2$ - $\text{CH}_4$  in different space and time.

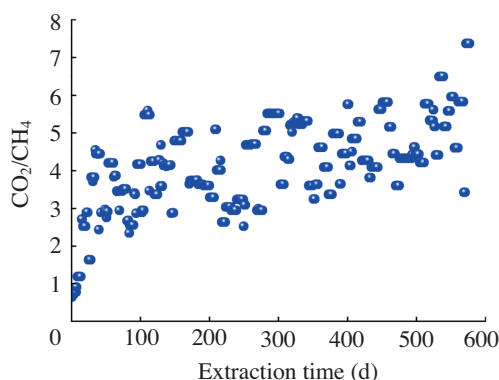


Fig. 6. Change of the ratio of  $\text{CO}_2$  and  $\text{CH}_4$  in gas by crossing boreholes extraction in the floor roadway with time.

#### 4. Time-spatial revolution of component fractionation with $\text{CO}_2$ - $\text{CH}_4$ by extraction

The Yaojie coalfield is the only mining area in China having both coal and  $\text{CO}_2$  outbursts.  $\text{CO}_2$  from external inorganic sources injected into the coal seam along the F19 fracture, showed similar characteristics to natural  $\text{CO}_2$  displacing  $\text{CH}_4$ , and  $\text{CO}_2$  is featured as the dominant gas in the coal seam near the injection point of the coal seam. The concentration of  $\text{CO}_2$  reduces, while the concentration of  $\text{CH}_4$  increases away from the F19 fracture. Geological exploration data show that the  $\text{CO}_2$  concentration ranges from 18.79% to 96.60% of the total gas content with an average of 81.83% in the eastern coal field. The  $\text{CH}_4$  concentration ranges from 0.48% to 68.79% of the total gas content. Other species are nitrogen, and hydrocarbon [18,19].

In order to prevent and control coal and  $\text{CO}_2$  outbursts, a regional gas control system is employed where the No.1 coal seam forms an upper protective coal seam in which mining, combined with pressure relief gas drainage of the protected coal seam, is used to control the gas in No.2 coal seam, thus eliminating the outburst hazard of the No.2 coal seam. This is shown in Fig. 5. In mining unloading conditions, the gas mixture in the No.2 coal seam is released by in the following ways: ventilation of the working face in the protective coal seam, gas extraction by pressure-relief in the floor roadway, ventilation of the working face in the protected coal seam. According to calculation, the ratio of application of the above ways is 15:2:3. This section mainly describes research on the ratios of  $\text{CO}_2$  and  $\text{CH}_4$  with the above different gas emissions pathways.

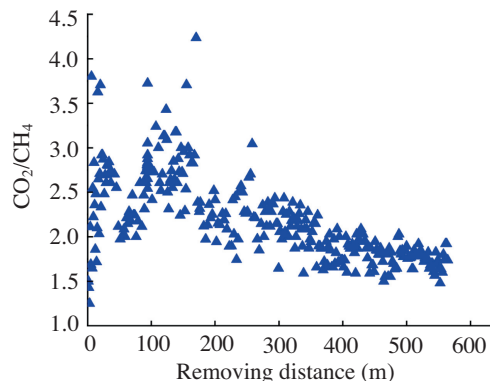


Fig. 7. Change of ratio of  $\text{CO}_2$  and  $\text{CH}_4$  by ventilation discharge with the 6213 working face removing in No.1 coal seam.

#### 4.1. Ratios of $\text{CO}_2$ to $\text{CH}_4$ in the extraction of gas by pressure-relief

During the extraction of coalbed gas in the Haishiwan Coal Mine, the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  in the gas mixture was obtained by regular monitoring of the gas concentration and extraction quantity in the main extraction pipeline, as shown in Fig. 6. The ratio of  $\text{CO}_2$  to  $\text{CH}_4$  ranges from 2.33 to 6.00, with an average of 3.93. With an increase in extraction time, the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  appears to increase. As the borehole drainage area is fixed, along with the extraction rate, the  $\text{CO}_2$  concentration gradually increases following pressure relief of the coal seam as  $\text{CH}_4$  desorbs and diffuses prior to  $\text{CO}_2$ . With increasing extraction time the  $\text{CH}_4$  desorption capacity gradually reduces, and  $\text{CO}_2$  desorption capacity increases relatively, which is consistent with the test results in Section 3.2.

#### 4.2. Ratios of $\text{CO}_2$ to $\text{CH}_4$ by ventilation discharge in No.1 coal seam

Based on a comparison of the  $\text{CO}_2$  and  $\text{CH}_4$  volumes in the ventilation discharge of 6213 working face, the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  first increases, then decreases as working face advance increases (Fig. 7). Over the first 150 m of 6213 working face advance, the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  increases rapidly, the ratio being between 2.5 and 4.0. With further working face advance, the ratio reduces gradually, showing a linear relationship. In general, the ratio is in the range 2.05–1.5. The regularity of change in the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  by ventilation discharge may be related to the following two factors:

- (1) The regularity of gas composition of 6223 working face, with advance of the working face from east to west. There is a greater proportion of  $\text{CO}_2$  in the coal seam of 6223 working face in the east which reduces gradually in a westward direction [20];
- (2) In the gas mixture, the density of  $\text{CO}_2$  is greater than that of air, whilst the density of  $\text{CH}_4$  is less than that of air. Therefore,  $\text{CH}_4$  has easier access to the working face of the No.1 coal seam under the action of negative pressure ventilation. In the case of gas extraction by pressure-relief,  $\text{CO}_2$  flows mainly through cross-measure boreholes in the floor roadway, and hence the volume of  $\text{CO}_2$  extracted by ventilation discharge reduces gradually.

#### 4.3. Ratios of $\text{CO}_2$ to $\text{CH}_4$ in ventilation discharge at 6223 working face

Fig. 8 shows the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  in ventilation discharge at 6223 working face. Despite the obvious difference in the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  in the original coal seam, the ratio of  $\text{CO}_2$  to  $\text{CH}_4$  in

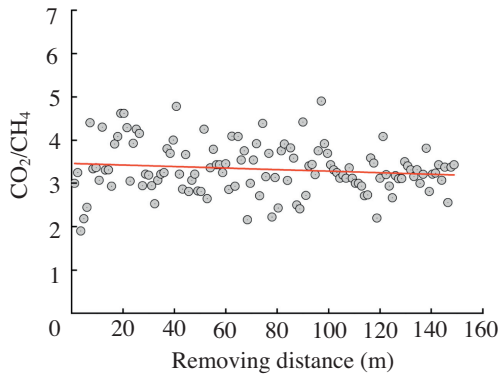


Fig. 8. Change of ratio of CO<sub>2</sub> and CH<sub>4</sub> by ventilation discharge with the 6223 working face removing in No.2 coal seam.

residual gas of the No.2 coal seam becomes steady at about 3.5 following gas extraction by pressure-relief.

According to the adsorption isotherms of pure CO<sub>2</sub> and CH<sub>4</sub>, tests on coals from Haishiwan Coal Mine produced ratios of CO<sub>2</sub> to CH<sub>4</sub> under different pressure conditions. With increasing equilibrium pressure, the ratio reduces gradually. When the ratio of CO<sub>2</sub> to CH<sub>4</sub> is 3.5, the equilibrium pressure is 0.3 MPa.

Studies on the adsorption–desorption behaviour of CO<sub>2</sub>–CH<sub>4</sub> mixtures on coals mostly focuses on adsorption–desorption laws in the laboratory [21,22]. As for the relation between gas migration in coal seams in time and space, research findings are much less common. Because of molecular dynamics differences in gas migration, the gas extracted desorbs and migrates according to certain rules in space and time, and the ratios of CO<sub>2</sub> to CH<sub>4</sub> are regular, which is consistent with component fractionation and which are in accord with the results of gas mixture desorption tests in the laboratory.

## 5. Conclusions

- (1) During the adsorption of gas mixtures on coals from Haishiwan Coal Mine, the variations in the CO<sub>2</sub> and CH<sub>4</sub> adsorption isotherm curves do not increase solely with increasing pressure; the excess volume of adsorbed gas decreases and then increases in the different components of CO<sub>2</sub> and CH<sub>4</sub>. It is significant that the ratios of CO<sub>2</sub> to CH<sub>4</sub>, are 9:1, 1:1, which shows that the adsorption capacities of CH<sub>4</sub> increase after CO<sub>2</sub> has been preferentially adsorbed, up to the point of saturation.
- (2) During the desorption process for binary gas mixtures on coals, in the adsorption phase, the concentration of CO<sub>2</sub> was always greater than that in the original gas mixture, whereas CH<sub>4</sub> shows the opposite characteristics. This illustrates that CO<sub>2</sub> has a greater adsorption ability and is preferentially adsorbed under different pressure conditions; in the free phase, the concentration of CO<sub>2</sub> is always less than that in the original gas mixture, but in contrast, the concentration of CH<sub>4</sub> is greater than that in the original gas mixture and shows that desorption of CH<sub>4</sub> precedes CO<sub>2</sub> and displays the competitive adsorption characteristics in the gas component separation graph.
- (3) During the process of mining the protective seam and gas extraction by pressure relief in Haishiwan Coal Mine, the ratio of CO<sub>2</sub> to CH<sub>4</sub> in the floor roadway appears to increase with increasing extraction time. With regard to gas control by ventilation discharge from the working face in No.1 coal seam, which is the protective layer, the ratio of CO<sub>2</sub> to CH<sub>4</sub> increases first, then decreases with further advance of the working face. In the gas captured by ventilation discharge

from the working face of No.2 coal seam, which is the protected layer, the ratio of CO<sub>2</sub> to CH<sub>4</sub> remains steady with advance of the working face, which is related to variations in the adsorption–desorption characteristics of CO<sub>2</sub>–CH<sub>4</sub> mixtures on coal, and differences in molecular dynamics and diversities of occurrence of CO<sub>2</sub> and CH<sub>4</sub>. The ratio of CO<sub>2</sub> to CH<sub>4</sub> in different gas extraction systems over different combinations of space and time, is consistent with the gas component fractionation results on gas mixtures on coal in the laboratory.

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