INTERNATIONAL JOURNAL OF HEAT AND TECHNOLOGY
Vol.33 (2015), No.3, pp.11-18
http://dx.doi.org/10.18280/ijht.330302

ADSORPTION EFFECT OF OVERLYING STRATA ON CARBON DIOXIDE IN COALFIELD FIRE AREA

Haiyan Wang[1,2*], Yafei Cheng[2] and Bo Yu[2]

[1]Hebei Mining Development and Safety Technology Lab, Tangshan, Hebei, 063009;
[2]Faculty of Mining & Safety Engineering, China University of Mining & Technology-Beijing, Beijing, 100083.

Email: whyhyp@163.com

ABSTRACT

This paper studied adsorption characters of rock (soil) on CO_2 at the states of pure CO_2 and $CO_2/N_2/CH_4$ ternary mixed gas. CO_2 adsorptive capacity of the rock (soil) decrease with the rise of temperature and decrease gradually till saturation condition, but increase with the rise of pressure. The adsorptive capacity of CO_2 falls along with shale, mudstone, sandy soil and sandstone. Moreover, the CO_2 adsorptive capacity is higher than that of CH_4 and N_2 obviously. With pressure rising, the CO_2 adsorptive capacity of rock (soil) increase slightly first and then remain steady. The ternary mixed gas tests show that as the CO_2 concentration in ternary mixed gas is the same, the mixing ratio of N_2 and CH_4 has little effect on the CO_2 adsorptive capacity. Based on the experimental results and Langmuir adsorption theory, an adsorption model of overlying rock (soil) toward CO_2 in coal fire area is put forward and then is used to evaluate the incomplete emission effect of CO_2 in Wuda coalfield fire area. The proportion of CO_2 adsorbed by the overlying rock (soil) in coalfield fire is 25% in maximum and the emission coefficient of CO_2 of Wuda coalfield fire area is ~75%.

Keywords: Coal fire, Carbon dioxide, Adsorption effect, Rock (soil).

1. INTRODUCTION

Changes of greenhouse gas (GHG) concentration in the atmosphere affect the global climate and environment at different time scales 1. Atmospheric warming caused by GHG has aroused wide concern in the world. United Nations Climate Change Conferences, which have been held many times in the past years, have set carbon emission reduction as the critical measure of dealing with global warming. Especially since Copenhagen Accord was concluded, it has become the topic for discussion that the participating countries shall try to reduce GHG emission actively. As the contracting party of United Nations Framework Convention on Climate Change, China also has international obligations to reduce GHGs.

Increase of GHG concentration in atmosphere results from the combined action of natural factors and human activities 2, therefore, we not only need to study how to eliminate GHG emission caused by human activities, but also need to study the contributions of natural factors on greenhouse effect, so as to acquire the effect law of GHG on atmospheric system objectively. Large area coal fire resulted from coal spontaneous combustion has become a serious natural disaster and distribute widely in the world, such as China, America, India, Indonesia, and so on. Hazards caused by coal fire also rouse concerns of relevant governments and scholars. China is the country with abundant coal resources in the world, with coal distributing more in the north and less in the south, among which over 80% concentrates in north and northwest 3. In the north and northwest of China, there are most of arid and semi-arid climate and the coal is buried shallow and thick. Moreover, exploitation of coal is in disorder. All of these have intensified spontaneous combustion of coal beds and formed large area coal fire areas. Influences of coal fire in north China on global environment have even caused the concerns of international communities and it has been described as global environmental and ecological disasters which might affect the 21st century significantly 4.

There is no doubt that coal fire could release plenty of GHG; however, it must be noted that the GHG released by coal fire must pass through the overlying rock (soil) system of coal bed as being emitted into the atmosphere. The overlying rock (soil) has adsorption effect on GHG. This means that the GHG generated by coal fire is not discharged to the atmosphere completely, i.e., such process is incomplete emission process. From the view of atmospheric environment protection, the more GHG of coal fire contained by the rock-soil system is , the less the GHG discharged into the atmosphere is. This is favorable for greenhouse effect reduction. The fruits related to coal system adsorbing GHGs (CO_2, CH_4, etc.) mainly centered in adsorption-descorption of CO_2 and CH_4 in the field of coal bed gas 5-8. There were also expressions on CO_2 adsorbtive capacity of shale (including carbonaceous shale) in some documents 910. Coal-bearing stratum is sedimentary rock which is mainly shale, sandstone, mudstone and limestone 11. GHGs generated by coal fire are mainly CO_2 and CH_4 1213. The adsorption effect of overlying rock (soil) toward these gases is a gas-solid adsorption process under the condition of high pressure and high temperature. However, there has little literatures on the adsorption effect of such process as well as the differences of GHG adsorption by different sedimentary rocks.

The objectives of our research are to test the adsorptive capacity of the overlying stratums samples (which extract from Wuda coalfield fire area in China) on CO_2 for pure CO_2 and $CO_2/N_2/CH_4$ ternary mixed gas at high temperature and high pressure, and to evaluate the influence of the overlying rock (soil) on GHG emission in coalfield fire area.

2. EXPERIMENTAL AND SAMPLES

2.1 Samples

Wuda region locates at ~E39°26′51″, N106°42′46″, 3.5 km away from the Yellow River in the east, 2km away from Wuhushan hill in the west. It is the intersection of Kubuqi, Maowusu and Wulan deserts. Experimental samples are taken from No.3 coalmine of Huayin Company, located in Wuda, Inner Mongolia. The samples are obtained from four stratums (sandy soil, sandstone, mudstone and shale, from surface to coalbed), which are outcrop obviously (See Figure 1). The samples collected in situ are put in sealed containers and taken to the laboratory. Then, they are smashed to particles and are sieved to 60 meshes, which are put into wide mouth bottle for experiment. The sample mass used in each adsorption test is 120 g. The basic parameters of the experimental samples are listed in Table 1.

Table 1. Basic parameters of samples

Samples	Particle size	Moisture (%)
Shale	60	2.11
Mudstone	60	1.96
Sandstone	60	1.24
Sandy soil	60	2.15

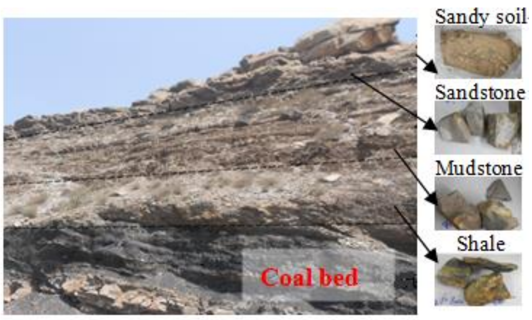

Figure 1. Stratum of the sampling site at coal fire area

2.2 Equipment and method

Selection of experimental pressure and temperature. Burning depth in the coalfield fire in north China are range from dozens of meters to over two hundred meters14 -16, but not more than 250m usually. Normal formation pressure gradient is 9.8-10.496 KPa/m 17. Therefore the experimental pressure range is set as 0.5-3.5Mpa with an interval of 1Mpa (namely, there are four pressure equilibrium points, i.e. 0.5Mpa, 1.5Mpa, 2.5Mpa and 3.5Mpa). The research and survey of coal spontaneous combustion in north China 18 showed that temperature of overlying strata ranged from normal to 300°C at different stages of coal fire. Thus, the experimental temperature is selected as 20-300°C. During the experiment, gas analysis is conducted every 20 °C (there are 15 temperature equilibrium points).

Determination of the proportion of absorbed gas. CO_2 has the largest proportion in all of GHGs during coal fire burning, followed by CH_4 19. Meanwhile, there also exists N_2 and other micro gases (such as CO) in the environment of coal fire. Our objective is to investigate the characteristics of overlying rock (soil) adsorbing CO_2. Thus, here ignores the influence of micro gases and observes the law of rock (soil) adsorbing CO_2 when there exist CH_4 and N_2. The adsorption experiment is preceded in two steps: (1) isothermal adsorption of pure CO_2, N_2, and CH4; and (2) adsorption of $CO_2/N_2/CH_4$ ternary mixed gas. For $CO_2/N_2/CH_4$ ternary mixed gas adsorption test, the volume proportion of N_2, CH_4 and CO_2 is set as: (1) N_2: CH_4:CO_2=20:20:60; (2) N_2: CH_4:CO_2= 50: 10:40; (3) N_2: CH_4:CO_2= 20:60:20%; (4) N_2: CH_4:CO_2=50:40:10.

The experimental system is shown in Figure 2. Adsorption experiment is finished by ISO-300 gas adsorption analyzer, made in TerracTek Company of USA. During experiment, open the control valve and the reference cylinder valve, and charge CO_2 and other gases into the experimental system; adjust the temperature of the reference cylinder to target temperature. When the temperature reaches the target and remains steady, the adsorption test procedure is started to collect time, pressure, temperature and other relevant data in the sample cylinder and the reference cylinder automatically. And the data are recorded as a file. According to the maturity and the quality of samples, the adsorption equilibrium time is determined as no less than 12 hours.

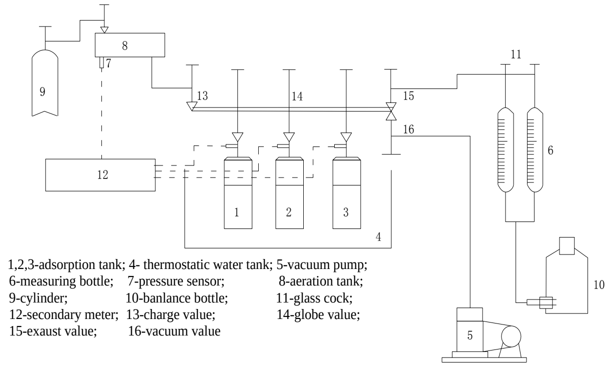

Figure 2. Gas adsorption analyzer system

3. RESULTS AND ANALYSIS

3.1 Influence of temperature and pressure on CO_2 adsorption

Figure 3 is the statistics of the adsorptive amount of samples on pure CO_2 at different pressures and temperatures. It showes that the CO_2 adsorptive capacity decrease with the rise of temperature and gradually reaches adsorption saturation. The adsorption of rock (soil) on CO_2 mainly is physical adsorption and an exothermic process. Thus, the

CO_2 adsorptive capacity of the samples at low temperature is much stronger. With the increase of pressure, CO_2 adsorptive amount of rock (soil) increases gradually. The basic law of the adsorption of rock (soil) toward CO_2 with temperature and pressure is similar to the relevant research results 20.

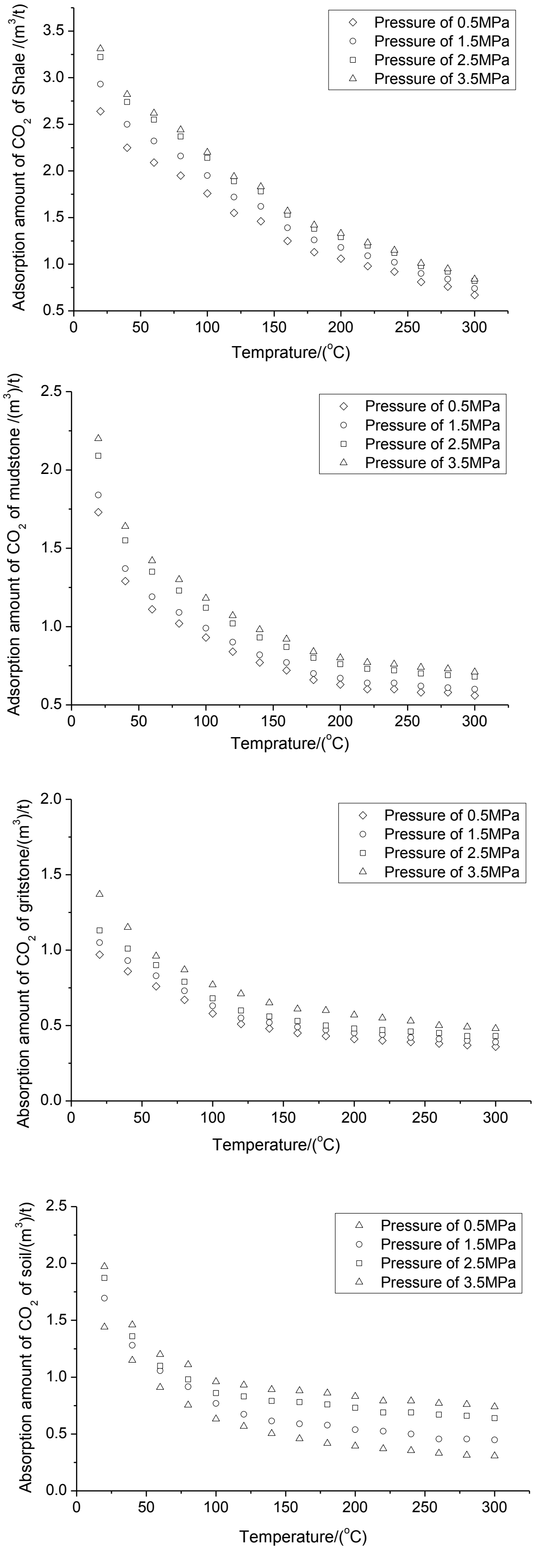

Figure 3. Adsorption of different samples on pure CO_2 (standard state)

For the same temperature and the pressure, the adsorptive amount of shale is larger than that of mudstone; the adsorptive amount of mudstone is larger than that of sandy soil, while the adsorptive amount of sandstone is the weakest. This character resultes from different maturity and porosity of the samples 21. The formation order of the sampling stratum in Wuda coalfield is shale, mudstone and sandstone. There exists stronger biomass and microbiological effects in sandy soil. Thus, besides the soil, the CO_2 adsorptive amounts of different samples are consistent with the formation time of the stratum, i.e. the closer to the coal bed is, the more CO_2 adsorptive capacity is.

Figure 4 is the comparison of adsorptive amounts of shale on pure CO_2, pure N_2 and pure CH_4. It showes that the adsorption quantity of rock on the three pure gases is $CO_2>CH_4>N_2$ and the adsorptive capacity of samples on CO_2 is significantly higher than that of CH_4 and N_2. Yi, et al 22, Zhang 23, et al. also obtained similar conclusion in tests of activated carbon and coal adsorbing CO_2, N_2 and CH_4. The critical temperatures of CO_2, CH_4 and N_2 are 31°C, -83°C and -147°C respectively. For the same temperature and pressure, the lower critical temperature of the gas is, the more difficult for solid adsorbing the gas is 24. Our research also showes that CO_2 has obvious adsorption competitive advantage than N_2 and CH_4. The lower the temperature is, the more obvious the advantage is. However, with the increase of pressure, the adsorption advantage of CO_2 increases slightly first and then retaines steady.

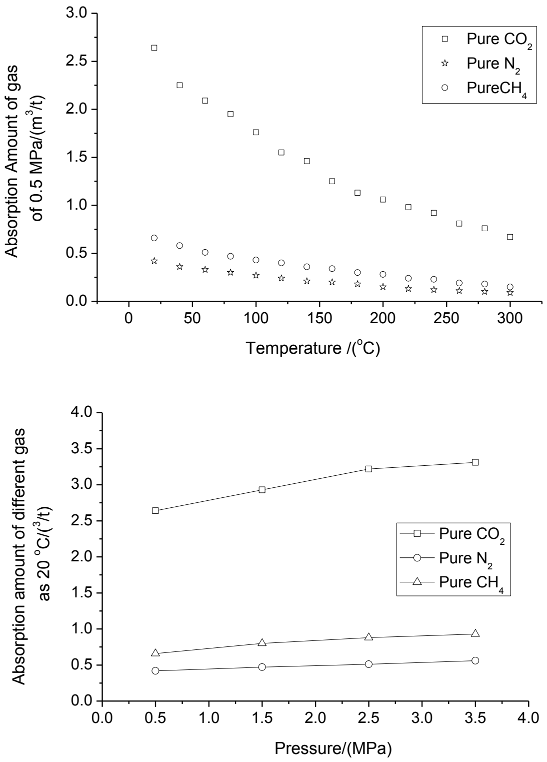

Figure 4. Adsorptive amount of shale on pure CO_2, N_2 and CH_4 (standard state)

3.2 Influence of CH_4/N_2 on CO_2 adsorption

In the ternary mixed gas experiment of GHGs, the shape of CO_2 adsorption curve is similar to that of pure CO_2 (see figure 5). The tendency of CO_2 adsorption with the changes of temperature and pressure is the same with that during pure CO_2 experiment. The adsorptive capacity of CO_2 decreases with the rise of the temperature and increases with the increase of the pressure. During the temary tests, the higher the CO_2 proportion is, the larger the CO_2 adsorption is. When the content of CO_2 decreases, the CO_2 adsorption curve is far away from the adsorption curve of pure CO_2.

Table 2 is the CO_2 adsorption quantity of shale at different mixed proportions of gases. It showes that for a fixed ratio of CO_2 in the mixed gas, the CO_2 adsorption with higher proportion of CH_4 is slightly lower than that with the higher proportion of N_2. Compared with CH_4, the competitive advantage of CO_2 to N_2 is larger than that of CO_2 to CH_4. Therefore, if the content of CH_4 is lower and the content of N_2 is higher, the adsorptive amount of CO_2 increases slightly. It's noted that the CO_2 adsorption quantity is determined not only by its adsorptive advantage, but also by the proportions of the gases mixed. Table 2 showes that with the increase of temperature and pressure, the difference of CO_2 adsorptive amount of two tests (N_2:CH_4:CO_2=20:60:20 and N_2:CH_4:CO_2=70:10:20) remaines 0.01-0.04 m^3/t, with average difference of ~0.028 m^3/t. In these two tests, the proportion of (N_2+CH_4) is 80% and that of CO_2 is 20%. Therefore, we can determine that if the proportion of CO_2 keeps invariant in ternary mixed gas, the proportion change of N_2 and CH_4 has little influence on the adsorptive amount of CO_2.

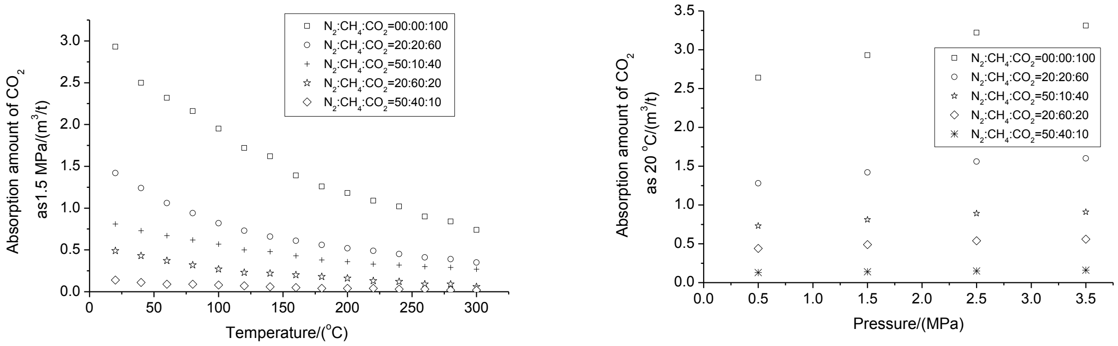

Figure 5. Adsorption amount of CO_2 in ternary mixed gas experiment (shale, standard state)

Table 2. CO_2 adsorptive amount of shale (standard state, m^3/t)

Temperature/ °C	N_2:CH_4:CO_2=20:60:20				N_2:CH_4:CO_2=70:10:20			
	0.5MPa	1.5MPa	2.5MPa	3.5MPa	0.5MPa	1.5MPa	2.5MPa	3.5MPa
20	0.44	0.49	0.54	0.56	0.44	0.49	0.54	0.57
40	0.39	0.43	0.47	0.48	0.4	0.45	0.49	0.51
60	0.34	0.37	0.41	0.42	0.36	0.4	0.43	0.44
80	0.29	0.32	0.35	0.36	0.31	0.36	0.39	0.39
100	0.25	0.27	0.3	0.31	0.28	0.31	0.34	0.35
120	0.21	0.23	0.25	0.26	0.25	0.27	0.3	0.3
140	0.2	0.22	0.24	0.25	0.22	0.26	0.29	0.27
160	0.18	0.2	0.22	0.23	0.2	0.24	0.25	0.25
180	0.16	0.18	0.19	0.2	0.19	0.21	0.22	0.22
200	0.15	0.16	0.18	0.18	0.18	0.18	0.21	0.21
220	0.12	0.13	0.14	0.15	0.16	0.17	0.18	0.18
240	0.1	0.12	0.13	0.13	0.14	0.15	0.17	0.17
260	0.08	0.09	0.1	0.1	0.11	0.12	0.14	0.12
280	0.08	0.09	0.1	0.1	0.11	0.11	0.14	0.11
300	0.06	0.06	0.07	0.07	0.08	0.08	0.1	0.09

4. ADSORPTION MODEL OF THE OVERLYING STRATA ON CO_2 IN COALFIELD FIRE AREA

4.1 CO_2 adsorption equation

During the process of coal fire developing, the adsorption of rock (soil) on burning products (CO_2, CH_4, N_2, etc.) belongs to gas-solid adsorption issue, which has the most commonly applied theory - Langmuir adsorption theory. According to Langmuir theory, the adsorption equation of rock (soil) on single component gas 25 can be described as follows

$$V = V_L \cdot \frac{P}{P_L + P} \tag{1}$$

Where V is the adsorptive capacity, m^3/t; P is the adsorption pressure, MPa; V_L is Langmuir volume coefficient; P_L is Langmuir pressure coefficient.

The experimental results of coal fire in situ and in laboratory 1213 show that CO_2 had the largest proportion in the GHGs produced by coal fire, followed by CH_4, while N_2

has the largest proportion among all the gas components. Our experimental results conclud that CH_4 and N_2 reduce the quantity of CO_2 adsorbed by the overlying strata because of the adsorption competition. Thus, Langmuir single component adsorption equation do not suitable for predicting the adsorption effect of the overlying rock (soil) on CO_2 directly. Extended Langmuir model retains all the consumed conditions of traditional Langmuir adsorption theory and considers that each component will conduct competitive adsorption at each active center. Therefore, here adopts the extended Langmuir model to investigate the adsorptive capacity of rock (soil) on CO_2 when there exist CH_4 and N_2. The adsorption model based on extended Langmuir equation is

$$V_i = \frac{V_{Li} b_i P_i}{1+\sum_{i=1}^{n} b_i P_i} \tag{2}$$

Where V_i is the adsorptive capacity of component i, m^3/t; V_{Li} is Langmuir volume coefficient of component i; b_i is Langmuir adsorption coefficient of component i, equals the reciprocal of Langmuir pressure coefficient, $1/P_{Li}$; P_i is the partial pressure of component i, MPa.

According to law of partial pressure, in the mixed gas, the partial pressure (P_i) of component i equals to the total pressure multiplied by the volume fraction (or mole fraction) of component i. Then, based on Eq. (2), the equation of calculating CO_2 adsorptive capacity of the overlying rock (soil) in the coal fire area is

$$V_{CO2} = \frac{V_{L,CO_2} y_{CO_2} P/P_{L,CO_2}}{1+\frac{y_{CO_2}P}{P_{L,CO_2}}+\frac{y_{CH_4}P}{P_{L,CH_4}}+\frac{y_{N_2}P}{P_{L,N_2}}} \tag{3}$$

Where V_{CO2} is CO_2 adsorptive capacity at multi-components, m^3/t; $V_{L,CO2}$ is Langmuir volume coefficient of pure CO_2; $P_{L,CO2}$, $P_{L,CH4}$, $P_{L,N2}$ are Langmuir pressure coefficient of pure CO_2, pure CH_4 and pure N_2; P is total pressure, MPa; y_{CO2}, y_{CH4}, y_{N2} are the volume fraction of CO_2, CH_4 and N_2 in the mixed gas.

It is needed to be explained that V_L and P_L in Eq. (3) have definite physical meanings. V_L represents the volume coefficient, and the smaller it's fitting value, the less the gas saturation adsorption capacity. P_L stands for the pressure coefficient, whose value relates with gas adsorption heat. The larger the P_L value, the smoother the isothermal adsorption curve of the gas. However, if achieving the real physical meanings of V_L and P_L, the pressure adopted in the adsorption test should reach a rather large range. It needs change from very low range of Henry's Law to the adsorption limit pressure of the gas. The pressure doesn't reach the state of adsorption saturated pressure in our study, for this reason, it is unnecessary to emphasize the physical meanings here. V_L and P_L are regarded as empirical constants merely.

According to the experimental data and Eq. (1), we regress the adsorptive capacity of pure CO_2, pure CH_4 and pure N_2 at different temperatures to acquire the V_L and P_L of single component (see Table 3). It showes that the fitting results are high correlation with the experimental results (R^2 were above 0.98). From Table 3, it can be seen that P_L around one certain constant with a small variation range with the rise of the temperature, while C_L decreases. Therefore, we apply nonlinear fitting to obtain the computational equation of C_L and regard P_L as a constant. The expression of C_L and the mean value of P_L regressed from the experimental results are all listed in Table 4. According to Table 4, the expression of V_L fitted from the four samples can be expressed as

$$V_L=a_1\ln t+a_2 \tag{4}$$

Where a_1 and a_2 are the two coefficients in fitted equation of V_L in Table 4.

Taking Eq. (4) into Eq. (3), the volume quantity of CO_2 absorbed by unit mass rock (soil) at standard state is

$$V_{CO2} = \frac{(a_1\ln(t)+a_2)\cdot y_{CO_2}\cdot P/P_{L,CO_2}}{1+\frac{y_{CO_2}P}{P_{L,CO_2}}+\frac{y_{CH_4}P}{P_{L,CH_4}}+\frac{y_{N_2}P}{P_{L,N_2}}} \tag{5}$$

Table 3. V_L and P_L of the shale

Temperature/°C	$V_{L,CO2}$	$P_{L,CO2}$	R^2	$V_{L,CH4}$	$P_{L,CH4}$	R^2	$V_{L,N2}$	$P_{L,N2}$	R^2
20	3.3790	0.1500	0.9951	0.9708	0.2494	0.9959	0.5587	0.1820	0.9878
40	2.8778	0.1493	0.9952	0.8605	0.2544	0.9968	0.4679	0.1643	0.9894
60	2.6753	0.1500	0.9952	0.7516	0.2505	0.9961	0.4295	0.1682	0.9871
80	2.4873	0.1478	0.9961	0.7013	0.2581	0.9968	0.3887	0.1635	0.9888
100	2.2441	0.1474	0.9952	0.6413	0.2574	0.9973	0.3597	0.1844	0.9869
120	1.9814	0.1490	0.9953	0.5828	0.2432	0.9952	0.3096	0.1622	0.9871
140	1.8678	0.1497	0.9951	0.5451	0.2745	0.9947	0.2834	0.1888	0.9925
160	1.6051	0.1521	0.9952	0.5065	0.2552	0.9979	0.2738	0.1995	0.9920
180	1.4509	0.1517	0.9956	0.4385	0.2457	0.9952	0.2398	0.1844	0.9869
200	1.3569	0.1497	0.9956	0.4196	0.2660	0.9949	0.1990	0.1778	0.9887
220	1.2582	0.1519	0.9952	0.3541	0.2533	0.9949	0.1797	0.2095	0.9862
240	1.1740	0.1478	0.9953	0.3321	0.2322	0.9970	0.1491	0.1332	0.9915
260	1.0295	0.1445	0.9960	0.2872	0.2625	0.9992	0.1393	0.1468	0.9903
280	0.9664	0.1458	0.9950	0.2601	0.2421	0.9914	0.1296	0.1635	0.9888
300	0.8579	0.1511	0.9943	0.2192	0.2457	0.9952	0.1199	0.1844	0.9869

Table 4. $C_{L,CO2}$ expressions and mean value of P_L to pure gas adsorption

Samples	$V_{L,\mathrm{CO2}}$		P_L		
	Fitted equation（t is temperature）	R^2	$P_{L,\mathrm{CO2}}$	$P_{L,\mathrm{CH4}}$	$P_{L,\mathrm{N2}}$
Shale	$V_{L,CO2}$= -0.974ln(t) + 6.5418	0.9727	0.15	0.253	0.174
Mudstone	$V_{L,CO2}$= -0.533ln(t) + 3.6588	0.9795	0.15	0.088	0.091
Sandstone	$V_{L,CO2}$= -0.323ln(t) + 2.2663	0.9872	0.18	0.144	0.39
Sandy soil	$V_{L,CO2}$= -0.595ln(t) + 3.7395	0.9625	0.146	0.166	0.457

Table 5. Comparison of predicted value and experimental value of CO_2 (CO_2:CH_4:N_2=40:10:50, shale)

Temperature /°C	P=0.5MPa			P=1.5MPa			P=2.5MPa			P=3.5MPa		
	Predicted value	Experimental value	Error	Predicted value	Experimental value	Error	Predicted value	Experimental value	Error	Predicted value	Predicted value	Error
20	0.89	0.83	0.01	0.94	0.81	0.15	0.99	0.89	0.11	1.0	0.91	0.09
40	0.73	0.65	0.12	0.77	0.73	0.05	0.87	0.80	0.09	0.9	0.85	0.06
60	0.68	0.61	0.11	0.71	0.67	0.07	0.8	0.74	0.05	0.87	0.76	0.14
80	0.63	0.56	0.13	0.67	0.62	0.07	0.72	0.68	0.06	0.81	0.73	0.1
100	0.60	0.51	0.18	0.64	0.57	0.12	0.70	0.63	0.11	0.68	0.64	0.06
120	0.50	0.45	0.11	0.52	0.50	0.04	0.62	0.55	0.13	0.63	0.57	0.11
140	0.48	0.43	0.12	0.53	0.48	0.11	0.54	0.52	0.04	0.60	0.54	0.11
160	0.43	0.39	0.11	0.46	0.43	0.07	0.50	0.47	0.12	0.5	0.49	0.02
180	0.38	0.35	0.08	0.40	0.38	0.05	0.48	0.42	0.14	0.49	0.43	0.14
200	0.35	0.33	0.08	0.38	0.36	0.04	0.45	0.40	0.12	0.46	0.41	0.12
220	0.35	0.30	0.15	0.37	0.33	0.11	0.39	0.36	0.08	0.4	0.38	0.1
240	0.27	0.28	-0.03	0.28	0.32	-0.13	0.33	0.35	-0.06	0.34	0.36	-0.07
260	0.25	0.27	-0.06	0.27	0.30	-0.11	0.31	0.33	-0.05	0.32	0.34	-0.06
280	0.25	0.26	-0.05	0.26	0.29	-0.11	0.31	0.31	0.00	0.31	0.32	-0.02
300	0.22	0.24	-0.06	0.24	0.27	-0.12	0.28	0.30	-0.05	0.29	0.31	-0.06

In order to observe the accuracy of Eq. (5), here selects the predicted value of CO_2 absorbed by rock (soil) to compare with the experimental value at CO_2:CH_4:N_2= 40:10:50 (see Table 5). The results show that the predicted value of CO_2 as the ternary adsorption are very close to the experimental value. These mean that the extended Langmuir equation can realize the computation of CO_2 adsorption capacity of rock (soil) well.

We regard the earth surface pressure as 0.1MPa and the formation pressure gradient as 9.8KPa/m, then the equilibrium pressure in Eq. (5) can be expressed as P=0.1+0.0098x (x is the depth away from earth surface, m). So the quantity of CO_2 adsorbed by single overlying stratum of the coal fire area is

$$G_{CO2} = S \cdot \rho \cdot h. \cdot \int_{x_1}^{x_2} \frac{1964 \times (a_1 \ln t + a_2) y_1 (0.1+0.0098\mathrm{x}) / P_{L,CO2}}{1 + \frac{y_{CO2}(0.1+0.0098\mathrm{x})}{P_{L,CO2}} + \frac{y_{CH4}(0.1+0.0098\mathrm{x})}{P_{L,CH4}} + \frac{y_{N2}(0.1+0.0098\mathrm{x})}{P_{L,N2}}} dx \tag{6}$$

Where G is the mass of CO_2 adsorbed by the stratum, g; t is temperature, °C; x is the depth of the stratum away from the earth surface, m; h is tthickness of the stratum, m; S is the projected area of the fire area on the surface, m^2; ρ is the density of the rock (soil), g/cm^3; 1964 is the coefficient of the volume of CO_2 converting into quality, the mole number of $1m^3$ gas is 22.4Kmol at the standard state, then the quality of $1m^3$ CO_2 at the standard state is 1000/22.4×44=1964g.

4.2 Emission coefficient of CO_2

Coal measures of Wuda coalfield is rather steady inclined strata with 23 coal seams (8 seams in Zhiluo formation, i.e 1#, 2#, 3#, 4#, 4_l#, 5#, 6#, and 7#, with the total thickness of 16.6 m and the coal bearing ratio of 15.4%; 15 seams in Yan'an formation, i.e. 8#, 9#, 10#, 11#, 12_u#, 12#, 13_{u3}#, 13_{u2}#, 13_{u1}#, 13#, 14#, 15#, 16#, 17# and 18#, with the total thickness of 20.7m and the coal bearing ratio of 9.4%). Most of roofs and floors of the coal seam are leveling. In 2012, the area of Wuda coal field fire area was about 239.6 hm^2 26. The densities of shale, mudstone, sandstone and sandy soil overlying the coal bed are $2.5g/m^3$, 2.55 g/cm^3, 2.6 g/cm^3 and 1.6 g/cm^3, respectively. The average thickness of shale, mudstone, sandstone and sandy soil are about 40m, 40m, 20m, and 1m. According to the observation value of surface temperature and coal spontaneous combustion temperature 2728 and the stratum heat transfer coefficient 29 30, the temperatures of shale, mudstone, sandstone and sandy soil strata are about 100 °C, 80 °C, 50 °C and 20 °C. The laboratory test of coal spontaneous combustion showes that the volume concentration of CO_2 generated by spontaneous combustion could reach as high as ~15% when coal fire reaches fully developing stage (~800°C 28). Correspondly, the volume concentration of N_2 is ~77% and that of CH_4 as high as 4%. Besides CO_2, N_2 and CH_4, during coal fire reaction, there also includ other gases, such as O_2, CO, etc, which are included in N_2 component in our paper. Thus, here selectes CO_2:CH_4:N_2=15:81:4. According to Eq. (6), the CO_2

adsorption quantity of the different overlying strata in Wuda fire area are shale with 55606t, mudstone with 16424t, sandstone with 5040t and sandy soil with 12t. Therefore, the total quantity of CO_2 adsorbed by the overlying strata is 77082t.

In the 23 coal beds of Wuda coalfield, 1#, 2#, 4#, 6#, 7#, 9#, 10#, 12# has coal fire. Based on the data of thickness of coal beds 31, the average thickness of coal fire existing is 7.06m 32. Based on the data of combustion efficiency of industrial bituminous coal 3334, the average combustion efficiency is estimated as 76.5%. The average density of coal in Wuda fire area is $1.53g/m^3$ 35, while the carbon content is 0.72 and the average coal remaining rate is 60%. And so, the CO_2 released by the coal in Wuda coalfield fire scope is calcu1ated as 313617t based on coal complete combustion law. Then, the proportion of CO_2 from coal combustion fixed by the overlying rock(soil) is 77082/313617=25% in the maximum. Namely, if we ignore CO_2 absorbed by coal beds and underground water, the emission coefficient of CO_2 released in Wuda coal field fire area is ~75%.

5. CONCLUSIONS

We design the experimental scheme on CO_2 adsorption of rock (soil) in coal fire area and obtain the CO_2 adsorption characters of the four samples (shale, mudstone, sandstone and sandy soil) at states of pure CO_2, pure N_2, pure CH_4 and their ternary mixed gas. Based on Langmuir gas-solid adsorption theory and the experimental results, the computational model of CO_2 adsorption amount of the overlying rock (soil) in coal fire area is put forward and is used to estimate the CO_2 emission coeffient of the Wuda coal field fire area.

ACKNOWLEDGEMENT

This research is supported by the National Science Foundation of China Program (No. 51304211), the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDA05030200) and Hebei Mining Development and Safety Technology Lab Program (No. 2013kykf02).

REFERENCES

1. J. D. Hakun, P. U. Clark, F. He, S. A. Marcott, A. C. Mix, Z. Liu, B. Otto-Bliesner, A. Schmittner and E. Bard, Global Warming Preceded by Increasing Carbon Dioxide Concentrations during the Last Deglaciation, *Nature*, vol.484, pp. 49-54, 2012. DOI: 10.1038/nature10915.
2. J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell and C. Johnson, Climate Change 2001: The Scientific Basis, Cambridge University Press, Cambridge, 2001.
3. D. Cao, X. Shi, X. Fan, C. Wu, Environmental Effect Analysis of Coalfield Fire, *China Mining Magazine*, vol.16, pp. 40-42, 2007.
4. Y. Lang, Hg and Greenhouse Gased Emission and Pollution in North China Coal Fire, *7th Proceedings of Environmental Chemistry of China*, 2013.
5. H. Yu, L. Zhou, W. Guo, Predictions of The Adsorption Equilibrium of Methane/Carbon Dioxide Binary Gas on Coals Using Langmuir and Ideal Adsorbed Solution Theory under Feed Gas Conditions, *International Journal of Coal Geology*, vol.73, pp.115-129, 2008. DOI:10.1016/j.coal.2007.03.003.
6. E. Yalcin, S. Durucan, Methane Capacities of Zonguldak Coals and The Factors Affecting Methane Adsorption, *Mining Science and Technology*, vol.13, pp.215-222, 1991. DOI: 10.1016/0167-9031(91)91346-J.
7. S. Bachu, Carbon Dioxide Storage Capacity in Uneconomic Coal Beds in Alberta, Canada: Methodology, Potential and Site Identification, *International Journal of Greenhouse Gas Control*, vol.1, pp. 374-385, 2007. DOI: 10.1016/S1750-5836(07)00070-9.
8. Z. Weishauptová, O. Přibyl, I. Sýkorová, Effect of Bituminous Coal Properties on Carbon Dioxide and Methane High Pressure Sorption, *Fuel*, vol. 139, pp.115-124, 2015. DOI: 10.1016/j.fuel.2014.08.030.
9. A. Busch, S. Alles, Y. Gensterblum, D. Prinz, D. N. Dewhurst and M. D. Raven, Carbon Dioxide Storage Potential of Shales, *International Journal of Greenhouse Gas Control*, vol.2, pp. 297-308, 2008. DOI: 10.1016/j.ijggc.2008.03.003.
10. P. Weniger, W. Kalkreuth, A. Busch and B. M. Krooss, High-Pressure Methane and Carbon Dioxide Sorption on Coal and Shale Samples from the ParanÁ Basin, Brazil, *International Journal of Coal Geology*, vol. 84, pp. 190-205, 2010. DOI: 10.1016/j.coal.2010.08.003.
11. D. Wang and Y. Wang, Coal Geology and Exploration Method, China University of Mining & Technology Press, Xuzhou, 1995.
12. C. Zhang, S. Guo, Y. Guan, B. Kong, J. Wu, J. Li, J. Wei, W. Duan, D. Cai, X. An and L. Kang, The Diffusion Area Simulation of Gases Released by Coal Fire, *Journal of China Coal Society*, vol. 37, pp.1698-1704, 2012.
13. A. E. Whitehouse and A. A. S. Mulyana, Coal Fires in Indonesia, *International Journal of Coal Geology*, vol. 59, pp.91-97, 2004. DOI: 10.1016/j.coal.2003.08.010.
14. Q. Zeng, Study on the Thermal Dynamic Characteristics of Combustion System for Coal Fires in Xinjiang Region, Ph.D Thesis, China University of Mining & Technology, Xuzhou, 2012.
15. D. Cao, X. Shi, X. Fan and G.Wang, Study on The Fractures Related with Coalfield Fire Area In Wuda Coalfield, Inner M ongolia, *Journal of China Coal Society*, vol. 34, pp.1009-1014, 2009.
16. Z. Song and C. Kuenzer, Coal Fires in China over the Last Decade: A Comprehensive Review, *International Journal of Coal Geology*, vol. 133, pp.72-99, 2014. DOI: 10.1016/j.coal.2014.09.004.
17. L. Wang, Well Control Technology of Underground Operating, Petroleum Industry Press, Beijing, 2007.
18. H. Guan, Coal Field Spontaneous Combustion Enviroment Investigation and Research in North China, China Coal Industry Publishing House, Beijing, 1998.
19. S. Liu, R. Wu, R. Li, Z. Hu and F. Song, Development and Application of a Device for CO_2 emission Flux Observation in Coal Spontaneous Combustion Zone, *Environmental Pollution and Control*, vol. 36, pp.32-42, 2014.
20. P. Baran, J. Cygankiewicz and K. Zarebska, Carbon Dioxide Sorption on Polish Ortholignite Coal in Low And Elevated Pressure, *Journal of CO_2 Utilization*, vol.3-4, pp.44-48, 2013. DOI: 10.1016/j.jcou.2013.09.003.
21. C. Ou, S. Li, M. Yi, P. Guo and L. Sun, Experimental Determination of Adsorption Isotherms of Gases in Three Reservoir Cores, *Acta Petrolei Sinica*, vol. 23, pp.72-76, 2002.
22. H. Yi, F. Li, P. Ning, X. Tang, J. Peng, Y. Li and H. Deng, Adsorption Separation of CO_2, CH_4 and N_2 on Microwave Activated Carbon, *Chemical Engineering Journal*, vol. 215-216, pp.635-642, 2013. DOI: 10.1016/j.cej.2012.11.050.
23. Z. Zhang, G. Liu, X. Zhang and X. Yang, Adsorption-disorption Experiments of CH_4 and CO_2 with Different Consistency, *Journal of China Coal Society*, vol. 34, pp. 551-554, 2009.
24. Y. X. Wang, W. Su, Y. P. Zhou, Adsorptive Separation

Properties of Activated Carbons with Different Pore Structures for CO_2, CH_4, N_2 and O_2, *Chem. Ind. Eng. Prog*, vol. 28, pp. 206-209, 2009.

25. R. Heller and M. Zoback, Adsorption of Methane and Carbon Dioxide on Gas Shale and Pure Mineral Samples, *Journal of Unconventional Oil and Gas Resources*, vol.8, pp.14-24, 2014. DOI: 10.1016/j.juogr.2014.06.001.
26. D. Cao, G. Yang, X. Dou, X. Song and M. Xiao, Calculation of Carbon Emission of Wuda coalfield fires in Inner Mongolia Based on Remote Sensing Technology, *Journal of China Coal Society*, vol.39, pp. 2489-2494, 2014.
27. S. B. Kroonenberg and X. Zhang, Pleistocene Coal Fires in Northwestern China, Energy for Early Man., One Million Years of Anthropogenic Global Environmental Change, *Proceedings of the ARA Symposium at the Royal Netherlands Academy of Art and Science*s *(KNAW)*, pp. 39-44, 1997.
28. J. Zhang, Study of Undergound Coal Fire and Its Prevention in China, China Coal Industry Publishing House, Beijing, 2008.
29. Y. Zhou, L. Gu, L. Li and L. Wu, Study on The Rock Thermal Conductivity Coefficient and Coal Thermal Property, *Energy Technology and Management*, vol.5, pp.134-143, 2011.
30. N. Qiu, Characters of Thermal Conductivity and Radiogenic Heat Production Rate in Basins of Northwest China, *Chinese Journal of Geology*, vol.37, pp.196-206, 2002.
31. D. Cao, X. Fan, H. Guan, Geological Models of Spontaneous Combustion in the Wuda Coalfield, Inner Mongolia, China, *Review in Engneering Geology*, XVIII, pp.23-30, 2007.
32. X. Du, S. Peng, H. Wang, S. Bernardes, G. Yang and Z. Li, Annual Change Detection by ASTER TIR Data and An Estimation of The Annual Coal Loss and CO2 Emission from Coal Seams Spontaneous Combustion, *Remote Sensing*, vol.7, pp. 319-341, 2015. DOI: 10.3390/rs70100319.
33. Q. Yu, Experimental Research on The Combustion Efficiency of Blended Coal Injection into BF, *Baosteel Technology*, vol.1, pp. 33-36, 1999.
34. H. Zeng, B. Yao, J. Qiu and Q. Yu, Studies of Combustion and Slagging Characteristics for Blended Coal with Anthracite and Bituminous, *Journal of Combustion Science and Technology*, vol.2, pp.181-189, 1996.
35. S. Li, R. Zhao and B. Zhang, Practice of Coal Blending for Suhaitu Coal Washing Plant, *Coal Cleaning*, vol.5, pp.35-37, 2003.