

## Limitations of measurements of supercritical CO<sub>2</sub> sorption isotherms on coals with manometric equipment – a theoretical description

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CO<sub>2</sub> adsorption isotherms on coals are important for estimating the CO<sub>2</sub> sequestration potential of coal beds and enhanced coalbed methane recovery using CO<sub>2</sub> injection into coal seams. This paper provides the characteristic of CO<sub>2</sub> compressibility factor and density change of CO<sub>2</sub> based CO<sub>2</sub> Equation of State. The paper investigates the effect of experimental pressure and its error, adsorption/desorption hysteresis, and coal swelling on measurements of supercritical CO<sub>2</sub> adsorption isotherms on coals with manometric equipment at high pressure. The results show that the characteristic density-change of CO<sub>2</sub> in proper pressure range determines great influence of experimental parameters, coal swelling and adsorption/desorption hysteresis on CO<sub>2</sub> adsorption on coal at high pressure. The effect of the hysteresis on sorption at high-pressure may leads to negative observed-adsorption. And coal swelling at high pressure has obvious effect on the precision and reproducibility of CO<sub>2</sub> adsorption. There are potential pitfalls of measurements of supercritical CO<sub>2</sub> adsorption isotherms on coals with manometric equipment at high pressure.

**Keywords:** Adsorption, CO<sub>2</sub>, coal, uncertainty, CO<sub>2</sub> sequestration.

### INTRODUCTION

CO<sub>2</sub> injection into coal bed has received increased attention as a potential option to reduce greenhouse gas CO<sub>2</sub> emissions to the atmosphere and to enhance the coalbed methane recovery (ECBM) [1]. Accurate measurements of CO<sub>2</sub> sorption isotherms on coals are vital for the optimum techniques of CO<sub>2</sub> sequestration and ECBM. For a given coal seam, sorption isotherm measurements provide information about the storage capacity, the overall economics of the process, and the types of operating conditions [2].

Much work has been carried out on the sorption capacity of coal with respect to CO<sub>2</sub> at low- and moderate pressure with manometric, volumetric, or gravimetric apparatus [3-10]. However, there have been very few high-pressure studies of CO<sub>2</sub>-coal sorption isotherms under in-seams conditions [11-20].

Unusual adsorption isotherms of CO<sub>2</sub> on coals at high pressure have been reported in the available literatures. Krooss et al. [11] performed CO<sub>2</sub>-sorption experiments on coals with manometric apparatus between 40 and 80 °C and pressures up to 20 MPa. The results of Krooss et al. [11] showed that all high-pressure CO<sub>2</sub> adsorption isotherms for moist samples were bimodal with distinct minima and even negative excess sorption values in the 8-10 MPa

range and beyond this range CO<sub>2</sub> adsorption capacity increased with increasing pressure. The strong bimodal character of the CO<sub>2</sub> excess isotherms on moist coals is interpreted as the result of a swelling effect caused by supercritical CO<sub>2</sub> and enhanced by water. Fitzgerald et al. [12] performed pure CO<sub>2</sub> adsorption on wet Tiffany mixed coal sample with volumetric apparatus at 327.6 K and pressures up to 14 MPa. The result of Fitzgerald et al. [12] showed that at high pressure (>7 MPa) the CO<sub>2</sub> Gibbs sorption capacity decreases with increasing pressure.

Coal swelling due to gas adsorption is a well-known phenomenon, and is used to correct adsorption isotherms for coal swelling [20-23]. Many researchers investigated the coal swelling with various ranks and experimental technique, and gave different conclusions. Reucroft et al. [24, 25] measured the swelling of various ranks of Kentucky coal by directly observing directional changes and found that the volume increase was between 0.36 and 4.18% at pressure from 0 to 1.5 MPa. Walker et al. [26] measured the expansion of powdered coals and macerals induced by CO<sub>2</sub> and found that expansion to an equilibrium value was fast and concluded that most of the CO<sub>2</sub> uptake was in open and closed (to He) micropores. Chikatamarla et al. [27, 28] measured CO<sub>2</sub> induced swelling on four coal samples with pressures up to 5.0 MPa and found that the volumetric strain at 0.6 MPa was from 0.26% to 0.66% for CO<sub>2</sub> and the volumetric strain and pressure can be described using a Langmuir like

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equation and the volumetric strain was approximately linearly proportional to the amount of gas adsorbed. St. George and Barakat [29] measured volumetric strains for adsorption at 4.0 MPa for CO<sub>2</sub> on a coal sample from New Zealand and found that the volumetric strain was 2.1% for CO<sub>2</sub>.

Pan and Connell [30] presented a theoretical model to describe adsorption-induced coal swelling. The developed model combines the two processes affecting coal volumetric changes, namely, swelling due to gas adsorption and matrix compression due to gas pressure. They found that the model was able to describe coal swelling behavior for the whole pressure range, including at very high gas pressure, where the coal swelling ratio may decrease after reaching a swelling maximum.

In order to better understand the variation in measured Gibbs-sorption of CO<sub>2</sub> with manometric technique at high pressure, this paper investigates the effect of the experimental parameters (including pressure and volume of two cells), adsorption/desorption hysteresis and volume swelling of coal on CO<sub>2</sub> adsorption. This main purpose of this paper is only to provide the general interpretations which the low repeatability and inter-laboratory reproducibility of CO<sub>2</sub> adsorption isotherm measurements, negative adsorption, unimodal isotherm is unavoidable due to the limitation of manometric measurement caused by the characteristic change of CO<sub>2</sub> compressibility factor or density at high pressure.

## MATERIALS AND METHODS

### Mass balance equation for CO<sub>2</sub> adsorption isotherm measurement

The increased Gibbs-sorption at equilibrium step  $i$  is calculated with mass balance of the amount of CO<sub>2</sub> transferred from the reference cell to the sample cell and the equilibrium amount of CO<sub>2</sub> in the sample cell. The increased Gibbs-adsorption ( $\Delta n_i^{\text{ex}}$  in mmol/g) at the end of  $i^{\text{th}}$  step is calculated by the real gas law shown in Eq. (1)

$$\Delta n_i^{\text{ex}} = \left( \frac{1}{RTm} \right) \left( V_R \left( \frac{P_{R,I}^i}{Z_{R,I}^i} - \frac{P_{R,F}^i}{Z_{R,F}^i} \right) - V_0 \left( \frac{P_{S,\text{Eq}}^i}{Z_{S,\text{Eq}}^i} - \frac{P_{S,\text{Eq}}^{i-1}}{Z_{S,\text{Eq}}^{i-1}} \right) \right) \quad (1)$$

where the subscripts, "I", "F" and "Eq", refer to the conditions in the cell before, final the gas expansion and adsorption equilibrium, the subscripts, "R" and "S" represent the reference and sample cell, the superscripts,  $i$  and  $(i-1)$  represent the  $i^{\text{th}}$  and  $(i-1)^{\text{th}}$  step, respectively,  $P$  is the pressure,  $Z$  is the compressibility factor of CO<sub>2</sub>,  $T$  is the temperature,  $R$  is the molar gas constant,  $m$  is the

mass of the coal sample,  $V_R$  and  $V_0$  is the volume of sample cell and the void volume in the sample cell, respectively.

The total Gibbs sorption in the sample cell at step  $j$  is the total amount exchanged with the reference cell for step 1 to  $j$ . The estimate of the total amount of excess adsorption ( $n_j^{\text{ex}}$ ) at the end of the  $j^{\text{th}}$  step is determined from Eq. (2)

$$n_j^{\text{ex}} = \Delta n_1^{\text{ex}} + \Delta n_2^{\text{ex}} + \dots + \Delta n_i^{\text{ex}} + \dots + \Delta n_j^{\text{ex}} \quad (2)$$

So, the Eq. (2) can be written from Eq. (3)

$$n_j^{\text{ex}} = \left( \frac{1}{RTm} \right) \left( V_R \sum_{i=1}^j \left( \frac{P_{R,I}^i}{Z_{R,I}^i} - \frac{P_{R,F}^i}{Z_{R,F}^i} \right) - V_0 \frac{P_{S,\text{Eq}}^j}{Z_{S,\text{Eq}}^j} \right) \quad (3)$$

The bulk density of CO<sub>2</sub> is a function of pressure and temperature, the amount of CO<sub>2</sub> exchanged is calculated from the difference in density in the reference cell between the charging and equilibrium

phase. If  $V_{Rm} = \frac{V_R}{m}$ ,  $V_{0m} = \frac{V_0}{m}$ ,  $\Delta \rho_R^i = \left( \frac{P_{R,I}^i}{Z_{R,I}^i} - \frac{P_{R,F}^i}{Z_{R,F}^i} \right) / RT$

,  $\Delta \rho_S^i = \left( \frac{P_{R,I}^i}{Z_{R,I}^i} - \frac{P_{R,F}^i}{Z_{R,F}^i} \right) / RT$ ,  $\rho_S^j = \frac{P_{S,\text{Eq}}^j}{RTZ_{S,\text{Eq}}^j}$ , the Eq.s (1)

and (3) can be written as shown in Eq.s (4) and (5),

$$\Delta n_i^{\text{ex}} = V_{Rm} \Delta \rho_R^i - V_{0m} \Delta \rho_S^i, \quad (4)$$

$$n_j^{\text{ex}} = V_{Rm} \left( \sum_{i=1}^j \Delta \rho_R^i - x \rho_S^j \right). \quad (5)$$

where  $V_{Rm}$  and  $V_{0m}$  is specific volume of reference cell and void volume of sample cell, respectively,  $\Delta \rho_R$  is density change of CO<sub>2</sub> in reference cell,  $\rho_S$  and  $\Delta \rho_S$  is density of CO<sub>2</sub> and its change in sample cell.

The equilibrium amount of CO<sub>2</sub> in the sample cell is the density at the equilibrium pressure and temperature multiplied by  $x$ , a volume ratio of void of sample cell and reference cell ( $V_0/V_R$ ). The Eqs. (4) and (5) can be written as the following,

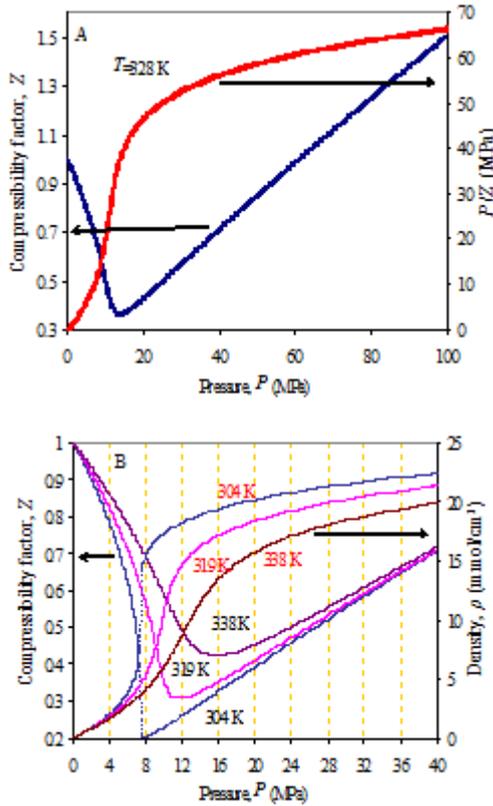
$$\Delta n_i^{\text{ex}} = V_{Rm} (\Delta \rho_R - x \Delta \rho_S), \quad (6)$$

$$n_j^{\text{ex}} = V_{Rm} \left( \sum_{i=1}^j \Delta \rho_R^i - x \rho_S^j \right). \quad (7)$$

### The compressibility factor and density

The change of compressibility factor and density with pressure. The independent variables for the excess adsorption are the initial and final pressure in the reference and sample cell, the empty and void volume of the reference and sample cell, the sample weight, and temperature. Also, the compressibility factor is another variable, whose value is dependent on the temperature and pressure. Although there is so many variables affecting the measured value of

CO<sub>2</sub> Gibbs adsorption, the compressibility factor ( $Z$ ) or density of CO<sub>2</sub> is the root of the effect at high pressure. The change of  $Z$ -factor and density of CO<sub>2</sub> are used to explain the limitation of measurements of supercritical CO<sub>2</sub> sorption with manometric apparatus at high pressure, the effect of other factors is investigated based on the change.



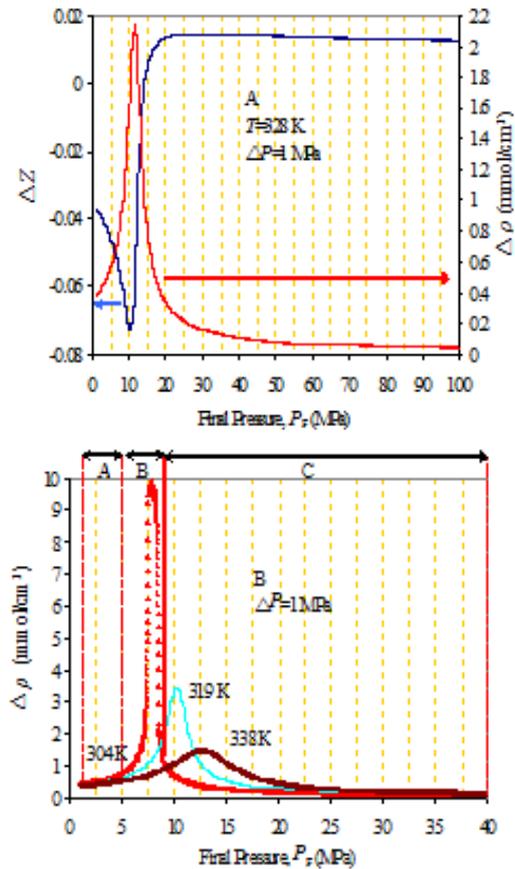
**Fig. 1.** The compressibility factor of CO<sub>2</sub> ( $Z$ ) and density of CO<sub>2</sub>, obtained from the Span and Wagner-EOS [31]

The compressibility factor ( $Z$ ) and the density ( $\rho$ ) of CO<sub>2</sub> were calculated at temperature from 31 °C to 65 °C and pressure up to 100 MPa based on the Span and Wagner Equation of State [31]. The  $Z$ - and  $P/Z$ -value at 55 °C and pressure up to 100 MPa (A) and the  $Z$ - and  $\rho$ -value at temperature of 31, 46, 65 °C and up to 40 MPa (B) is shown in Fig. (1).

Just as shown in Fig. (1A), the  $Z$ -values decrease to 0.3647 from 1 at a pressure of 13.62 MPa, and increase from 0.3647 to 1.504 at 100 MPa and 55 °C. It is known that CO<sub>2</sub> at pressures up to 100 MPa have increasing  $P/Z$ -value with the pressure increase (Fig. 1A).

It can be seen from Fig. (1B) that all  $Z$ -factors of CO<sub>2</sub> are unimodal with distinct minima in the 8-16 MPa range, which is dependent on the temperature. There is the range of a pressure ( $P_{\min}$ - $P_{\max}$ ) corresponding the minimum of  $Z$ -factor ( $Z_{\min}$ ) because the limit of error for calculated  $Z$ -factor

based on the Span and Wagner Equation of State is 0.0001. The  $Z_{\min}$  and its corresponding pressure ( $P_{\min}$  or  $P_{\max}$ ) increase with the increase of temperature. Table 1 gives the minimum  $Z$ -factor and its corresponding pressure range at from 31 to 65 °C.



**Fig. 2.** The CO<sub>2</sub> compressibility factor and density change at 328 K and pressure up to 100 MPa (A) and comparison of density change at 304, 319 and 338 K and pressure up to 40 MPa (B), with pressure change of 1.0 MPa.

The unimodality and minimum of CO<sub>2</sub>  $Z$ -factor determine the shape of CO<sub>2</sub> density isotherms as shown in Fig. (1B). The density-values increase sharply with the increasing pressure and decreasing  $Z$ -factor as pressure below “valley” pressure ( $P_{\min}$ ) corresponding minimum  $Z$ -factor ( $Z_{\min}$ ), and increase smoothly with the increasing  $Z$ -factor and pressure at pressure of more than the  $P_{\min}$ . For example, the density of CO<sub>2</sub> increases sharply at pressure of less than 13.62 MPa and 55 °C, and increases smoothly at pressure of more than 13.62 MPa. Table 1 gives also the density range of CO<sub>2</sub> corresponding  $P_{\min}$  and  $P_{\max}$  at the temperature of from 31 to 65 °C.

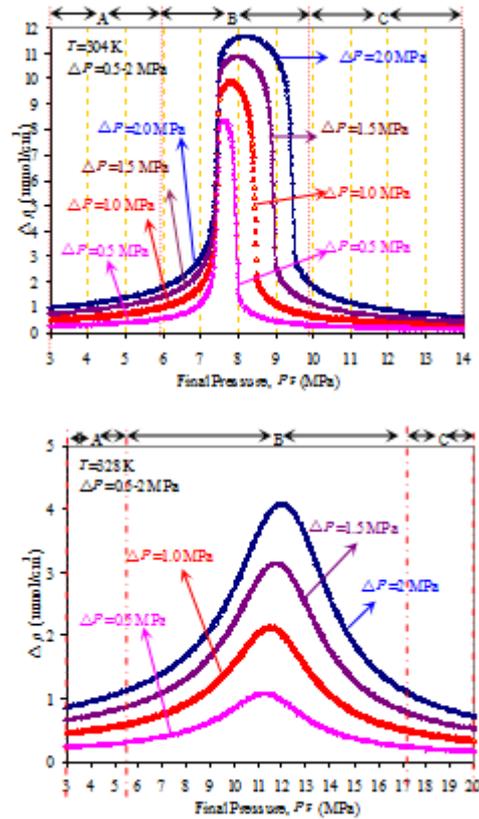
**The density change with pressure at a constant temperature.** The change of bulk density of CO<sub>2</sub> is used to calculate the Gibbs sorption based Eq. (5) or

(7). The Fig. (2) shows the change of density of CO<sub>2</sub>,  $\Delta\rho$ , with pressure-change ( $\Delta P$ ), of which Fig. (2A) gives the  $\Delta\rho$  with  $\Delta P$  of 1.0 MPa at 55 °C and pressure of up to 100 MPa, Fig. (2B) gives it with  $\Delta P$  of 1.0 MPa at temperature of 31, 46 and 65 °C and up to 40 MPa. The  $\Delta\rho$  with  $\Delta P$  of 0.5, 1.0, 1.5 and 2.0 MPa at temperature of 31 °C (A) and 55 °C (B) is shown in Fig. (3).

It can be seen from Fig. (2) that the density changes exhibit a three-stage tendency with the pressure increase. Although the change increases at low pressure and decreases at high pressure with the pressure increases, the change is comparatively small compared with that at medium pressure. The density change ( $\Delta\rho$ ) increase first and then decrease with pressure increase at medium pressure, and the maximum  $\Delta\rho$  is achieved at a pressure. The maximum  $\Delta\rho$  and its corresponding pressure is expressed as  $\Delta\rho_{\max}$  and  $P_{\max}$ , respectively. The  $\Delta\rho_{\max}$  decreases and  $P_{\max}$  increases with the temperature increase.

The change of bulk density of CO<sub>2</sub> is used to calculate the Gibbs sorption based Eq. (5) or (7). The Fig. (3) shows the change of density of CO<sub>2</sub>,  $\Delta\rho$ , with various pressure-change ( $\Delta P=0.5, 1.0, 1.5$  and  $2.0$  MPa) at temperature of 31 °C (A) and 55 °C (B).

The density-change curve can be divided into three regions (i.e. A, B and C) based on its value and corresponding final-pressure as seen in Fig. (3). Because of  $\rho_{R,I}^i > \rho_{R,F}^i, \rho_{S,Eq}^i > \rho_{S,Eq}^{i-1}$ , it should be noted that the final pressure ( $P_F$ ) in Fig (3) means the initial pressure of reference cell ( $P_{R,I}^i$ ) or equilibrium pressure of sample cell ( $P_{S,Eq}^i$ ). The region A at relatively low pressure and region C at relatively high pressure are of small  $\Delta\rho$  values with the pressure change, and the region B at high pressure are great  $\Delta\rho$ -values. The pressure ranges of region B increase with increase of temperature and  $\Delta P$ , as shown in Fig. (3). The highest  $\Delta\rho$ -value and its corresponding pressure in region B at temperature of from 31 °C to 65 °C is given in Table 1.



**Fig. 3.** The change density of CO<sub>2</sub> and dividing region with change of pressure 0.5, 1.0, 1.5 and 2.0 MPa at temperature of 304 K (A) and 328 K (B).

**The density change with temperature at a constant pressure:** A CO<sub>2</sub> Excess-sorption isotherm describes the CO<sub>2</sub> amount on coal at the equilibrium pressure at constant temperature. So, the CO<sub>2</sub> density change with temperature at a constant pressure ( $[\partial\rho/\partial T]_p$ ) is expressed with that the pressure as the  $x$ -axis and the density-change as the  $y$ -axis under different temperatures, as shown in Fig. (4).

It can be seen from Fig. (4) that the density changes still exhibits a three-stage tendency with the pressure increase, and CO<sub>2</sub> density decreases with temperature increase. The effect of temperature on density-change decreases with temperature increase. Although the change increases at low pressure and decreases at high pressure with the pressure increases, the decrease of density change is comparatively small compared with that at medium pressure. The decrease of density change increases first and then decreases with pressure increase at medium pressure, and the maximum  $-[\partial\rho/\partial T]_p$  is achieved at a pressure.

**Table 1.** The minimum Z-factor ( $Z_{\min}$ ) and its corresponding pressure ( $P_{\min}$ ,  $P_{\max}$ ) and density range ( $\rho_{\min}$ ,  $\rho_{\max}$ ), and maximum change of CO<sub>2</sub> density ( $\Delta\rho_{\max}$ ) with different pressure change ( $\Delta P$ ) and its corresponding final-pressure ( $P_F^i$ ) at temperature of from 31 °C to 65 °C.

T (°C)	Z-factor minimum, its pressure and density				Density change and its final pressure with different pressure change								
	$Z_{\min}$	Pressure range (MPa)		Density range (mmol/cm <sup>3</sup> )		$\Delta P=0.5$ MPa		$\Delta P=1.0$ MPa		$\Delta P=1.5$ MPa		$\Delta P=2.0$ MPa	
		$P_{\min}$	$P_{\max}$	$\rho_{\min}$	$\rho_{\max}$	$\Delta\rho_{\max}$	$P_F^i$	$\Delta\rho_{\max}$	$P_F^i$	$\Delta\rho_{\max}$	$P_F^i$	$\Delta\rho_{\max}$	$P_F^i$
31	0.2047	7.9	7.95	15.269	15.365	8.357	7.60	9.864	7.81	10.880	8.01	11.668	8.18
32	0.2120	8.14	8.25	15.141	15.346	7.649	7.77	9.333	9.97	10.430	8.20	11.271	8.39
33	0.2192	8.41	8.51	15.080	15.259	6.921	7.96	8.795	8.18	9.980	8.37	10.871	8.56
34	0.2264	8.65	8.80	14.968	15.228	6.207	8.12	8.252	8.33	9.523	8.55	10.464	8.79
35	0.2335	8.91	9.05	14.901	15.135	5.523	8.29	7.713	8.51	9.061	8.74	10.060	8.91
36	0.2405	9.21	9.26	14.906	14.987	4.887	8.46	7.181	8.68	8.607	8.88	9.654	9.11
37	0.2476	9.40	9.58	14.729	15.011	4.323	8.62	6.671	8.84	8.157	9.06	9.250	9.26
38	0.2545	9.69	9.79	14.724	14.876	3.832	8.79	6.181	9.00	7.717	9.22	8.849	9.47
39	0.2614	9.95	10.03	14.673	14.791	3.410	8.94	5.719	9.19	7.289	9.38	8.455	9.58
40	0.2683	10.17	10.31	14.565	14.766	3.057	9.10	5.293	9.32	6.877	9.56	8.073	9.79
41	0.2751	10.42	10.55	14.508	14.689	2.758	9.24	4.902	9.49	6.482	9.72	7.700	9.94
42	0.2819	10.63	10.82	14.398	14.655	2.503	9.41	4.546	9.66	6.114	9.88	7.338	10.10
43	0.2886	10.87	11.06	14.335	14.586	2.289	9.56	4.225	9.81	5.764	10.04	6.991	10.26
44	0.2952	11.15	11.26	14.331	14.472	2.102	9.81	3.935	9.95	5.439	10.17	6.662	10.40
45	0.3018	11.38	11.51	14.261	14.424	1.942	9.85	3.675	10.11	5.136	10.33	6.349	10.55
46	0.3084	11.56	11.79	14.132	14.414	1.805	10.00	3.442	10.25	4.856	10.49	6.050	10.69
47	0.3148	11.87	11.95	14.172	14.267	1.684	10.16	3.233	10.40	4.596	10.65	5.770	10.84
48	0.3213	12.02	12.25	14.017	14.285	1.576	10.27	3.045	10.55	4.359	10.76	5.507	10.99
49	0.3276	12.32	12.41	14.047	14.149	1.481	10.45	2.875	10.66	4.139	10.93	5.259	11.17
50	0.3340	12.46	12.72	13.891	14.181	1.396	10.55	2.721	10.80	3.937	11.05	5.029	11.27
51	0.3402	12.73	12.89	13.890	14.065	1.321	10.73	2.582	10.97	3.750	11.22	4.812	11.44
52	0.3464	12.96	13.10	13.845	13.995	1.252	10.86	2.454	11.10	3.579	11.35	4.609	11.60
53	0.3526	13.13	13.37	13.738	13.989	1.190	10.01	2.339	11.22	3.421	11.50	4.420	11.75
54	0.3587	13.35	13.58	13.689	13.925	1.133	11.23	2.233	11.35	3.275	11.62	4.245	11.85
55	0.3647	13.62	13.73	13.694	13.805	1.082	11.26	2.135	11.53	3.138	11.76	4.081	11.98
56	0.3707	13.83	13.94	13.639	13.747	1.034	11.44	2.044	11.64	3.013	11.88	3.926	12.14
57	0.3767	13.97	14.22	13.516	13.758	0.991	11.56	1.961	11.74	2.895	12.03	3.781	12.27
58	0.3826	14.18	14.43	13.467	13.704	0.952	11.66	1.884	11.84	2.786	12.17	3.646	12.38
59	0.3884	14.45	14.56	13.478	13.580	0.915	11.80	1.813	12.06	2.684	12.30	3.519	12.51
60	0.3942	14.66	14.76	13.432	13.523	0.881	11.84	1.747	12.22	2.590	12.39	3.400	12.62
61	0.4000	14.78	15.04	13.306	13.540	0.849	11.99	1.685	12.33	2.501	12.49	3.288	12.77
62	0.4057	14.98	15.24	13.256	13.486	0.819	12.19	1.629	12.40	2.418	12.63	3.182	12.90
63	0.4113	15.30	15.31	13.315	13.324	0.792	12.33	1.574	12.53	2.340	12.72	3.082	13.06
64	0.4170	15.33	15.67	13.120	13.411	0.766	12.47	1.523	12.69	2.267	12.87	2.988	13.18
65	0.4225	15.58	15.79	13.122	13.298	0.742	12.58	1.476	12.79	2.197	13.40	2.900	13.30

## DISCUSSION

In order to construct an adsorption isotherm of CO<sub>2</sub> on coal, the increasing pressure is repeated for incrementally increasing the pressure of CO<sub>2</sub> in sample cell,  $P_{S,Eq}^i > P_{S,Eq}^{i-1}$ . A portion of CO<sub>2</sub> is transferred from the reference cell to the sample cell, at this point,  $P_{R,I}^i > P_{R,F}^i$ . In case of positive adsorption,

$P_{S,Eq}^i > P_{S,Eq}^{i-1}$  and  $P_{R,I}^i > P_{R,F}^i$  do hold. Consequently, the CO<sub>2</sub>  $\rho$ -values in two cells increase with equilibrium pressure increasing in the sample cell, just as shown in Fig. (1),  $\rho_{R,I}^i > \rho_{R,F}^i, \rho_{S,Eq}^i > \rho_{S,Eq}^{i-1}$ . We regard the initial pressure in reference cell ( $P_{R,I}^i$ ) and equilibrium pressure in sample cell ( $P_{S,Eq}^i$ ) as the final pressure ( $P_F$ ) of pressure change ( $\Delta P$ ). The  $P_F$

is used for the pressures of two cells in the regions (A, B and C), as shown in Fig. (3).

Theoretically, the excess sorption of CO<sub>2</sub> can be calculated from Eqs. (1) and (2). The incremental Gibbs-adsorption ( $\Delta n_i^{ex}$ ) is zero or positive if no adsorbed CO<sub>2</sub> is desorbed during CO<sub>2</sub> expansion from reference cell into sample cell. However, the change characteristic of CO<sub>2</sub> density as shown in Fig. (2), may be result in the negative incremental Gibbs-adsorption, just discussed in the following text.

From Eq. (4), the relation between the CO<sub>2</sub> density change ratio in the two cells ( $\Delta\rho_S^i/\Delta\rho_R^i$ ) and the void volume ratio of two cells ( $V_R/V_S$ ), involves three case, i.e. (1)  $\Delta\rho_S^i/\Delta\rho_R^i = V_R/V_S$  for zero adsorption increment ( $\Delta n_i^{ex}$ ), (2)  $\Delta\rho_S^i/\Delta\rho_R^i < V_R/V_S$  for positive  $\Delta n_i^{ex}$  and (3)  $\Delta\rho_S^i/\Delta\rho_R^i > V_R/V_S$  for negative  $\Delta n_i^{ex}$ . The  $V_R/V_S$  value is constant for a manometric setup, known coal and its mass, and the changed volume caused by coal swelling. The  $V_R/V_S$  values are between 0.2 and 2 from the published references. A smaller volume of reference cell or lower  $V_R/V_S$  value is not favorable to raise the pressure in the sample cell.

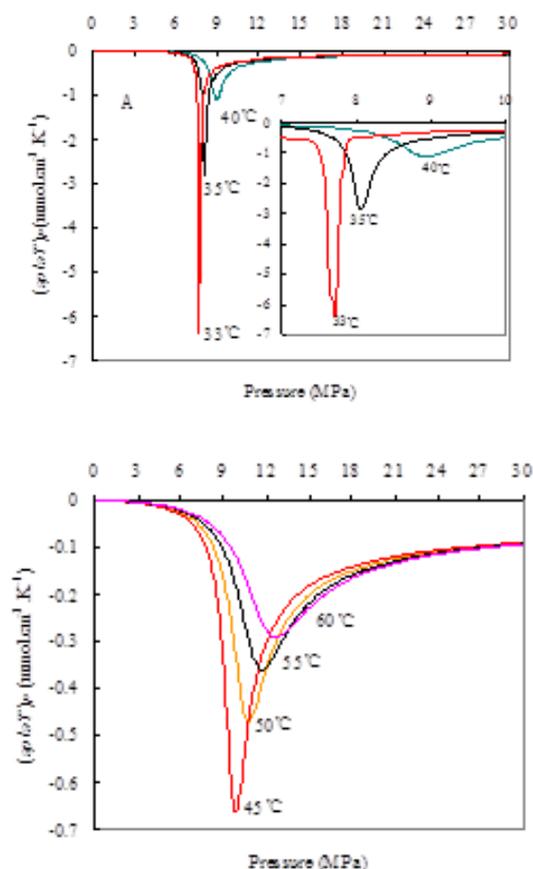


Fig. 4. The comparison of CO<sub>2</sub> density change with temperature at constant pressure

### Effect of pressure on CO<sub>2</sub> Gibbs sorption isotherm

(1) In case that both the final pressures of two cells are in region A as shown in Fig. (3),  $P_{R,I}^i$  and  $P_{S,Eq}^i$  are obviously less than the final pressure ( $P_F^i$ ) with the maximum density-change ( $\Delta\rho_{max}$ ) as shown in Table 1. In this case, the adsorption isotherm of CO<sub>2</sub> can be obtained at low and moderate pressure, which is dependent on the temperature. We must take into account two cases in case of region A. ( I ) The adsorption of CO<sub>2</sub> on coal in sample cell at low pressure determine  $V_{Rm}\Delta\rho_R > V_{0m}\Delta\rho_S$  from Eq. (4), and is described with Langmuir. The small  $\Delta\rho_R$  and  $\Delta\rho_S$  in region A decide hold of  $V_{Rm}\Delta\rho_R > V_{0m}\Delta\rho_S$  in case of  $V_{Rm} > V_{0m}$ . The adsorption of CO<sub>2</sub> on coal lead to  $\Delta P_R > \Delta P_S$  and  $\Delta\rho_R > \Delta\rho_S$  in case of  $V_{Rm} < V_{0m}$ , which make  $V_{Rm}\Delta\rho_R > V_{0m}\Delta\rho_S$  hold. ( II ) As CO<sub>2</sub> adsorption reaches approximately maximum (saturation), the  $\Delta P_R$ -value is not obvious greater than  $\Delta P_S$  as the CO<sub>2</sub> adsorption increment is smaller. Although there is  $P_{R,I}^i > P_{S,Eq}^i$  in this case, the adsorption is constant with the pressure as  $V_{Rm}\Delta\rho_R \approx V_{0m}\Delta\rho_S$ .

Currently, most investigators carried out studies of CO<sub>2</sub> sorption on coal adsorption, which focused on the experimental pressure in region A. This also explains why the sorption isotherm reported by Goodman et al. [32] had good reproducibility for different independent laboratories at temperatures of either 22 °C or 55 °C and pressures up to 7 MP.

(2) In case  $P_{R,I}^i$  is in region B and  $P_{S,Eq}^i$  is in region A, in which the adsorption isotherm of CO<sub>2</sub> can be obtained at moderate and high pressure. In this case, the density change in reference cell is obviously higher than that in sample cell, i.e.  $\Delta\rho_R > \Delta\rho_S$ . The measured CO<sub>2</sub>-adsorption like the saturation sorption in the case of (1), but the measuring error of CO<sub>2</sub> sorption caused by measurement error of volume and pressure in reference cell is great. The reproducibility of CO<sub>2</sub> Gibbs sorption is mainly dependent on the measurement error of pressure and volume as the great density change in this case. As there is a saturation-adsorption, the expansion CO<sub>2</sub> from reference cell mainly increases the density of bulk CO<sub>2</sub> in sample cell, and the equilibrium pressure of sample cell should increase to the pressure in region B.

(3) In case that both the final pressure of reference and sample cell are in region B, in which the sorption isotherm of CO<sub>2</sub> can be obtained at high

pressure. The measured adsorption like that of case (2) except that the measurement error of adsorption is great with the pressure errors of two cells. The negative sorption increment and bad reproducibility of CO<sub>2</sub> Gibbs sorption may be obtained with the pressure and volume errors of two cells as the greater  $\Delta\rho_R$  and  $\Delta\rho_S$  with the same  $\Delta P$  in this case.

(4) In case that the final pressure of reference cell is in region C and the final pressure of sample cell is in region B, in which the adsorption isotherm of CO<sub>2</sub> can be obtained at high pressure. The obvious negative sorption increment may be obtained with the pressure and volume errors of sample cell and great  $\Delta\rho_S$  with the same  $\Delta P$  in this case.

(5) In case both the final pressure of reference and sample cell is in region C, in which the adsorption isotherm of CO<sub>2</sub> can be obtained at high pressure. In this case, the increased-adsorption is not distinct as  $\Delta\rho_R \approx \Delta\rho_S$  with the same  $\Delta P$ .

No distinct difference in density change of CO<sub>2</sub> with pressure at low and moderate pressure determine better repeatability and small error for CO<sub>2</sub> sorption isotherms with manometric equipment. The distinct CO<sub>2</sub> density change in sample or reference cell with pressure at high pressure determine that it is difficult to measure CO<sub>2</sub> sorption isotherms with better repeatability and small error, which will be discussed in the following text.

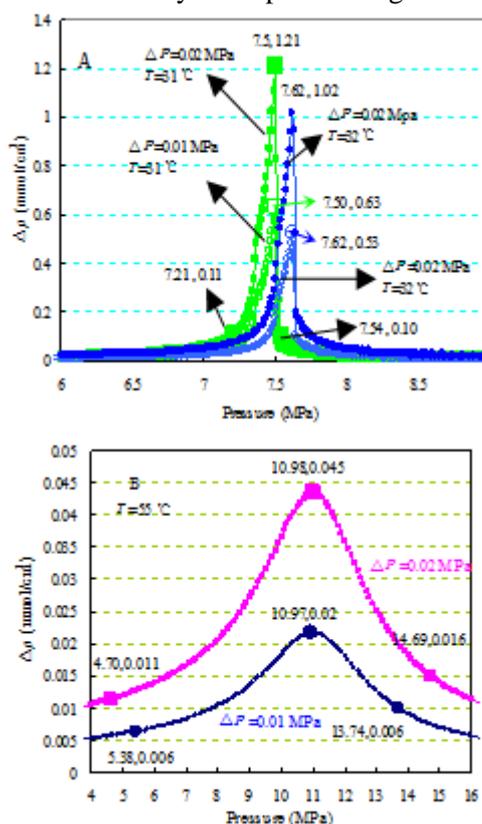
To minimize the effect of the measurement error of pressure on CO<sub>2</sub> adsorption, the pressure range in reference cell should be controlled in region A or C, rather than B region. The initial pressure in the reference cell is controlled by the charged amount with syringe pump, and the final pressure is controlled by the transferred portion of CO<sub>2</sub>. That is, the experimental procedures involve the cases (1), (4) or (5) described above, which is used to construct the adsorption in low, moderate and high pressure, respectively.

#### Effect of the measurement error of pressure

The estimation of the error with respect to each independent variable about CO<sub>2</sub> adsorption measurement is not the scope of this paper. The adsorption error caused by measurement error of pressure in region B is investigated as the density change is greater than that in region A and C with the same  $\Delta P$ . This main purpose of the analysis about the measurement error of pressure is only to provide an explanation for the negative incremental Gibbs-adsorption and less repeatability, which may be caused by the error of pressure at appropriate pressure range.

Although the pressure transducers have accuracy from  $\pm 0.001$  to  $\pm 0.01$  MPa, the reading is generally accurate to  $\pm 0.01$  MPa. The reading error of 0.01 MPa and 0.02 MPa are employed to estimate its effect on CO<sub>2</sub> density.

The Fig. (4) shows the density change of CO<sub>2</sub> ( $\Delta\rho$ ) for the pressure change ( $\Delta P$ ) of 0.01 and 0.02 MPa at temperature 31, 32 and 55 °C. The temperature obviously affects  $\Delta\rho$  for the same  $\Delta P$  at proper pressure, in which the changed-density maximum is 1.21, 0.63 and 0.045 mmol/cm<sup>3</sup> for 0.02 MPa increased-pressure at 31, 32 and 55 °C, respectively, and it is 0.63, 0.53 and 0.02 mmol/cm<sup>3</sup> for  $\Delta P$  of 0.01 MPa at 31, 32 and 55 °C, respectively. The maximum error caused by the pressure error mainly takes place in region B.



**Fig. 5.** The change density of CO<sub>2</sub> with change of pressure 0.01 MPa and 0.02 MPa at 31, 32 °C (A) and 55 °C (B) obtained from the Span and Wagner-EOS. Positions on the curves are identified as (a, b) where a and b are the pressure and its density change with the pressure change

The density change due to the error of pressure reading causes the bad accuracy of excess adsorption and exceptional Gibbs sorption of CO<sub>2</sub> at proper pressure, such as negative adsorption. As a portion of CO<sub>2</sub>,  $\Delta n_R$  mmol, is transferred from the reference cell to the sample cell and both cells are allowed to

equilibrate. The density error is 1.21 mmol/cm<sup>3</sup> and 0.63 mmol/cm<sup>3</sup> for the error of pressure reading of 0.02 and 0.01 MPa at equilibrium pressure of 7.5 MPa and 31 °C. If the specific volume of sample cell or void volume of sample cell is 1 cm<sup>3</sup>/g-coal, the negative adsorption of 1.21 mmol/cm<sup>3</sup> and 0.63 mmol/cm<sup>3</sup> at 31 °C will be obtained due to pressure reading-error of 0.02 and 0.01 MPa in reference cell at  $P_{Eq,I}^i$  of 7.5 MPa or in -0.02 and -0.01 MPa in sample cell at  $P_{R,I}^i$  of 7.5 MPa. However, when the  $P_{Eq,I}^i$  or  $P_{R,I}^i$  is 7.21 MPa at 31 °C, the pressure error of 0.02 MPa in sample cell or -0.02 MPa in reference cell will result in negative adsorption of 0.11 mmol/g. When the  $P_{Eq,I}^i$  or  $P_{R,I}^i$  increases from 7.5 MPa to 7.54 MPa at 31 °C, the negative adsorption error caused by pressure error of 0.02 MPa decreases from 1.21 mmol/g to 0.10 mmol/g. So, the influence range of the pressure error on adsorption is narrow. The effect of pressure error on adsorption decrease with temperature increase, and the influence range of the error get wide.

#### Adsorption/desorption hysteresis

The clear negative effect of temperature on the adsorption capacity [11] made the CO<sub>2</sub> desorption from coal as increase of temperature. The adsorption/desorption hysteresis isotherm was observed for pure CO<sub>2</sub> [7, 8, 19, 21, 33-37]. The desorption isotherm generally lies to the upside of the adsorption one, which mean at the same equilibrium pressure the CO<sub>2</sub> adsorption obtained in the process of pressure increase is lower than it obtained in the course of pressure decrease.

Construction of the adsorption isotherms of CO<sub>2</sub> on coal requires the expansion of gas from reference cell into sample cell. During the gas expansion procedure, the temperature was increased or decreased in the two cells as a result of the Joule-Thompson effect [31]. During the gas expansion, the temperature was decreased in the reference cell as CO<sub>2</sub> is expanded in this cell, while it was increased in sample cell as CO<sub>2</sub> is compressed in this cell. However, at equilibrium, both temperatures were reached the temperature of the water bath. 5 minutes was satisfactory for reaching the thermal equilibrium [9].

The portion CO<sub>2</sub>-adsorption on coal may desorbed from coal as the temperature of sample cell increase in the course of CO<sub>2</sub> expansion from the reference cell to sample cell. The Adsorption/desorption hysteresis determines the portion of desorbed CO<sub>2</sub> can not be adsorbed when the temperature of sample cell decrease with

reaching the thermal equilibrium. The CO<sub>2</sub> adsorption is so great that the desorbed CO<sub>2</sub> caused by the adsorption/desorption hysteresis can not be observed at low and moderate pressure, however, the hysteresis may result in the negative adsorption because of no or less sorption increment at high pressure.

#### Coal volume swelling

According to Ozdemir et al. [21], the uncertainties in volume estimations include nascent volume created by the swelling or shrinkage of solid adsorbent ( $\Delta V_c$ ), the over- or underestimation of the void volume due to adsorption of He and/or the extra volume due to the sieving effect ( $\Delta V_0$ ), the volume change due to the dissolution of the adsorbing gas ( $\Delta V_d$ ), and so forth. So, the change in the void volume in the sample cell ( $\Delta V_x$ ) is  $\Delta V_x = \Delta V_c \mp \Delta V_0 \mp \Delta V_d$ .

In case of the void volume correction term in step  $i$  ( $\Delta V_x^i$ ), the realistic adsorption increment ( $\Delta n_{i,R}^{ex}$ ) can be obtained from Eq.s (8) and (9) based on Eq.s (1) and (4),

$$\Delta n_{i,R}^{ex} = \left( \frac{1}{RTm} \right) \left( V_R \left( \frac{P_{R,I}^i}{Z_{R,I}^i} - \frac{P_{R,F}^i}{Z_{R,F}^i} \right) - \left( V_0 - \Delta V_x^i \right) \left( \frac{P_{S,Eq}^i}{Z_{S,Eq}^i} - \frac{P_{S,Eq}^{i-1}}{Z_{S,Eq}^{i-1}} \right) \right), \quad (8)$$

$$\Delta n_{i,R}^{ex} = V_{Rm} \Delta \rho_R^i - (V_{0m} - \Delta V_x^i) \Delta \rho_S^i. \quad (9)$$

The measured adsorption increment ( $\Delta V_x^i$ ) is lower than the realistic adsorption increment ( $\Delta n_{i,R}^{ex}$ ) based on Eq.s (4) and (9). If a volume ratio of void of sample cell and reference cell in case of volume correction ( $x_i' = (V_0 - \Delta V_x^i)/V_R$ ), the Eq. (6) can be written to

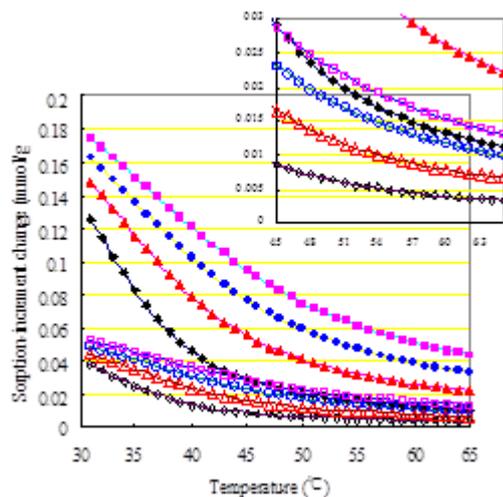
$$\Delta n_{i,R}^{ex} = V_{Rm} (\Delta \rho_R - x_i' \Delta \rho_S). \quad (10)$$

Coal swelling of 2-3% has been observed at CO<sub>2</sub> pressures of 1 MPa [25]. Although the degree of coal swelling was measured in low pressure, coal swelling is dependent on CO<sub>2</sub> pressure. At moderate to high pressure, coal swelling may result in significant errors in measurements of CO<sub>2</sub> adsorption on coals using gas adsorption techniques that work well with rigid solids. With a manometric apparatus, the coal swelling will change the ratio of container volume to sample volume [20]. St. George and Barakat [29] had been observed that an initial contraction occurred due to the hydrostatic pressure before expansion due to CO<sub>2</sub> adsorption.

We do not investigate the effect of coal swelling on CO<sub>2</sub> adsorption at low pressure. Volume

change due to coal swelling is only investigated at moderate and high pressure in this paper. As the equilibrium pressure of sample is in region B as shown in Fig. (3), the density change is much large that the effect of coal swelling on measured-adsorption is great and the adsorption obvious decrease. The negative CO<sub>2</sub>-adsorption will be obtained in this case.

Based on Eq. (9), the realistic CO<sub>2</sub>-sorption increment is dependent on the correction volume ( $\Delta V_x^i$ ), specific volume of two cells ( $V_R, V_0$ ) and the density change of bulk CO<sub>2</sub> in two cells ( $\Delta\rho_R, \Delta\rho_S$ ). The effect of volume change ( $\Delta V_x$ ) will get small in case of  $\Delta V_x^i \ll \Delta V_{0m}$  based on Eq. (9), which means great volume of sample cell in comparison with coal volume (i.e. small mass of coal sample).  $\Delta V_x^i \ll \Delta V_{0m}$  can be obtained with control the experimental parameters. The coal swelling of 2-3% and small  $\Delta\rho_S$  at low and moderate pressure (in region A) slightly affect the CO<sub>2</sub> adsorption in case of  $\Delta V_x^i \ll \Delta V_{0m}$ , but the great  $\Delta\rho_S$  in region B still make great error of CO<sub>2</sub> adsorption, especially negative adsorption.



**Fig. 6.** Gibbs adsorption change of CO<sub>2</sub> for specific void-volume decrease of 0.015 cm<sup>3</sup>/g-coal (open symbols) and 0.05 cm<sup>3</sup>/g-coal (closed symbols) and the pressure-change of 0.5 MPa (◇, ◆), 1.0 MPa (△, ▲), 1.5 MPa (○, ●) and 2.0 MPa (□, ■) at a pressure corresponding the maximum density-change and temperature from 31 to 65 °C

The coal swelling of 0.25-10% is equivalent to the volume increase of  $1.67 \times 10^{-3}$ - $6.67 \times 10^{-2}$  cm<sup>3</sup>/g-coal in case of the coal density of 1.5 g/cm<sup>3</sup>. The specific void-volume increase of 0.015 and 0.05 cm<sup>3</sup>/g-coal (the coal swelling of 2.25 and 7.75%) and the pressure change ( $\Delta P$ ) of 0.5, 1.0, 1.5 and 2.0 MPa in sample cell are used to investigate the effect of coal swelling on adsorption change maximum.

$\Delta\rho_S \Delta V_x$  is calculated with  $\Delta V_x$  of 0.015 and 0.05 cm<sup>3</sup>/g-coal and  $\Delta\rho_S$ -value at temperature from 31 to 65 °C and  $\Delta P$  of 0.5, 1.0, 1.5 and 2.0 MPa as shown in Table 1, which expresses the maximum of CO<sub>2</sub> adsorption increase caused by coal swelling of 2.25 and 7.75%. Fig. (6) shows the maximum of CO<sub>2</sub> adsorption increase as a function of temperature and coal swelling of 2.25 and 7.75%.

The effect of coal swell on sorption increment reduces with experimental temperature increase. As the coal swelling of 2.25%, the sorption-increment change is 0.01-0.05 mmol/g-coal at equilibrium-pressure increment of 2.0 MPa, and 0.003-0.04 mmol/g-coal at the increment of 0.5 MPa at the temperature from 31 to 65 °C. As the coal swelling of 7.75%, the change is 0.01-0.13 and 0.04-0.18 mmol/g-coal at pressure increment from 0.5-2.0 MPa and the temperature from 31 to 65 °C. Although the decreasing value of sorption increment due to coal swell of 2-3% is small, the effort of this on sorption isotherm is noticeable as error propagation of each step of sorption.

In case of without regard to coal swelling, which is adopted with rigid solid, the CO<sub>2</sub> adsorption on coal get small in comparison with realistic value and the decrease is dependent on temperature, pressure, swelling amount and specific void-volume of sample cell. The decrease of CO<sub>2</sub> adsorption may lead to the negative adsorption under proper conditions, such as equilibrium pressure in region B and small specific void-volume in sample cell. As shown in Fig. (6), the coal swelling effect on the adsorption decrease with the increase of experimental temperature.

The Gibbs adsorption change of CO<sub>2</sub> on coal is the function of temperature, the coal swelling amount, the pressure change amount in sample and equilibrium pressure of CO<sub>2</sub>. It is noted that with the coal swelling amount obtained at low pressure, the large correction is underestimated at the high pressures because the coal swelling decrease as the CO<sub>2</sub> pressure dropped [20]. The effect of coal swelling on adsorption mainly takes place in the larger density change, which is dependent on temperature and equilibrium pressure of CO<sub>2</sub>.

## CONCLUSIONS

This study provides the idea about limitation of measurements of supercritical CO<sub>2</sub> adsorption isotherms on coals with manometric equipment at high pressure. The characteristic density-change of CO<sub>2</sub> in proper pressure range determines great influence of experimental parameters on measured adsorption of CO<sub>2</sub> on coal at high pressure. Unusual adsorption isotherms of CO<sub>2</sub> on coals may be

obtained with manometric technique at proper pressure range (high pressure), which is from 8 to 16 MPa and is dependent on the temperature. The experimental parameters include volume of two cells, coal mass, error of pressure and volume and coal swelling. The error of pressure and volume in two cells may result in the less reproducibility and repeatability of CO<sub>2</sub> adsorption on coals at high pressure because of great change of CO<sub>2</sub> density. The experimental parameters and their errors may result in negative sorption increment and even negative adsorption. The coal swelling may result in negative adsorption. Without consideration of measurement error of pressure and volume, the influence of experimental parameters and coal swelling, the adsorption isotherm of CO<sub>2</sub> on coal obtained with manometric equipment at high pressure can not express accurately the CO<sub>2</sub> sorption capacity on coal.

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## ОГРАНИЧЕНИЯ НА ИЗМЕРВАНИЯТА НА СВРЪХКРИТИЧНИТЕ ИЗОТЕРМИ ЗА СОРБЦИЯ НА CO<sub>2</sub> ВЪРХУ ВЪГЛИЩА С МАНОМЕТРИЧНО ОБОРУДВАНЕ - ТЕОРЕТИЧНО ОПИСАНИЕ

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(Резюме)

Изотермите на адсорбция на CO<sub>2</sub> върху въглищата са важни за оценката на потенциала за улавяне на CO<sub>2</sub> на въглищните пластове и подобрената регенерация на метан от въглища чрез впръскване на CO<sub>2</sub> във въглищните пластове. Тази статия представя характеристиката на коефициента на свиваемост на CO<sub>2</sub> и изменението на плътността на CO<sub>2</sub>, базирано на CO<sub>2</sub> уравнението на състоянието. Статията изследва ефекта на експерименталното налягане и неговата грешка, хистерезис на адсорбция / десорбция и набъбване на въглищата върху измерванията на изотермите на суперкритична CO<sub>2</sub> адсорбция върху въглища с манометрично оборудване при високо налягане. Резултатите показват, че характерната промяна на плътността на CO<sub>2</sub> в подходящия диапазон на налягането определя голямо влияние на експерименталните параметри, набъбване на въглищата и хистерезис на адсорбция / десорбция върху адсорбцията на CO<sub>2</sub> върху въглища при високо налягане. Ефектът на хистерезиса върху сорбцията при високо налягане може да доведе до отрицателна наблюдавана адсорбция. Набъбването на въглищата при високо налягане има очевиден ефект върху точността и възпроизводимостта на адсорбцията на CO<sub>2</sub>. Съществуват потенциални клопки за измерване на изотермите на свръхкритична CO<sub>2</sub> адсорбция върху въглища с манометрично оборудване при високо налягане.