



ERRORS OF MANOMETRIC CO₂ SORPTION EXPERIMENTS ON COAL CAUSED BY ACCURACY OF PRESSURE SENSOR

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Abstract- The accuracy of supercritical CO₂ sorption determination on coal is important for estimating the CO₂ sequestration potential of coal bed using CO₂ injection into deep unminable coal seams. Based on the CO₂ density change and CO₂ sorption data of three selected coal samples, this paper investigates the effect of pressure-sensor accuracy on measurements of CO₂ adsorption isotherms on coals with manometric equipment. The characteristic density-change of CO₂ in proper pressure range determines a greater influence of pressure error on CO₂ adsorption data on coal. The sensor accuracy has significant influence on Excess sorption increment of CO₂ on coal in medium pressure (7-12 MPa), and on CO₂ Excess-sorption isotherm at medium- and high pressure. The medium pressures with a greater CO₂ density-change at a constant temperature in the sample cell are probably inevitable. A lower experiment-temperature will results in a greater measurement error of the sorption caused by pressure sensor accuracy. The pressure sensor accuracy may result in the less reproducibility and repeatability of CO₂ adsorption on coals at medium- and high pressure, and negative sorption increment and even negative adsorption.

Index terms: Pressure sensors, Measurement errors, Carbon dioxide, Sorption, Coal, Experimental uncertainty, Pressure effects, Manometers.

I. INTRODUCTION

The injection of CO₂ into deep unminable coal seams has received increased attention as a very attractive option to sequester greenhouse gas CO₂ and to enhance the coalbed methane recovery (ECBM) [1]. Accurate measurements of CO₂ adsorption isotherms on coals are vital for the optimum development of techniques to sequester CO₂ with an enhancement of CH₄ recovery [2, 3].

For the determination of CO₂ adsorption on coal, three different techniques are commonly used in terms of the physical parameters, namely the manometric, volumetric and gravimetric methods [4]. The manometric method is most widely used for determining gas sorption capacities on coal. In the manometric technique, the adsorption isotherms are obtained by calculating the adsorbed amount of gas from an appropriate gas equation at each equilibrium pressure [5]. The setup typically consists of calibrated reference and sample cells, and temperature and pressure sensors. Goodman et al. [4, 6] gave an important and interesting study, which provided a guidance for estimating the reproducibility of sorption isotherms on coals from different laboratories under low [6] and high [4] pressure. They provided the first inter-laboratory comparison of CO₂ isotherm measurements for coals at temperatures of either 22 °C or 55 °C and pressures up to 7 MPa. The differences among the data sets among the laboratories agreed better at low- and medium pressure [6]. Then, they investigated the inter-laboratory reproducibility of CO₂ isotherm measurements on coals among six independent laboratories at 55 °C and pressures up to 15 MPa [4]. Agreement among the laboratories was good up to 8 MPa, the data among the laboratories diverged significantly for two of the laboratories and coincided reasonably well for four of the laboratories at the higher pressures, Yu et al. [7] investigated the reasons that CO₂ sorption diverged significantly among the laboratories at high pressure, provided by Goodman et al. [4]. They demonstrated that the experimental parameters for manometric equipment affect the CO₂ isotherms at high pressure. Gensterblum et al [8] also investigated CO₂ Excess sorption isotherms on coals among three European laboratories. Their results showed that the deviations between the CO₂ isotherms of the different laboratories were higher at high-pressure than that at low-pressure.

Several researchers have discussed a wide range of potential sources of error in determination of sorption [9-14], including experimental parameters and indexes of coal quality. In the

manometric procedure, pressure sensors are connected to the sample and reference cells, and the error of the sensor significantly affects the determination accuracy of CO₂ sorption isotherm. Although the sorption error caused by pressure measurement was calculated with propagation error, there has not been a detailed investigation of the effect of the accuracy of the pressure sensor on the sorption determination.

In order to better understand the variation in measured Excess-sorption of CO₂ with manimometric technique at high pressure, this paper investigates the effect of the pressure error on CO₂ sorption determination. This main purpose of this paper is only to provide the general interpretations which the effect of the pressure sensor accuracy of manometric apparatus on sorption isotherm of CO₂ on coal at high pressure. The error of sorption determination caused by pressure sensors are addressed here in some detail.

II. THEORY

a. Mass Balance Equations for Sorption Measurement

The increment of Excess sorption at equilibrium step i is calculated with mass balance of the amount of CO₂ transferred from the reference cell to the sample cell and the equilibrium amount of CO₂ in the sample cell. The increment of Excess sorption (Δn_i^{ex} in mmol/g) at the end of i^{th} step is calculated by

$$\Delta n_i^{\text{ex}} = \left[V_R (\rho_{R,I}^i - \rho_{R,F}^i) - V_0 (\rho_{S,\text{Eq}}^i - \rho_{S,\text{Eq}}^{i-1}) \right] / m, \quad (1)$$

where m is the mass of the coal sample, g; $\rho_{R,I}^i$ and $\rho_{R,F}^i$ is the CO₂ density in the reference cell before and final the CO₂ expansion in i^{th} step, respectively, mmol/cm³; $\rho_{S,\text{Eq}}^i$ and $\rho_{S,\text{Eq}}^{i-1}$ is the CO₂ density in the sample cell at adsorption equilibrium i^{th} and $(i-1)^{\text{th}}$ step, respectively, mmol/cm³; V_R and V_0 is the volume of reference cell and the void volume in the sample cell, respectively, cm³.

The total Excess sorption at step j (n_j^{ex} in mmol/g) is

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

If $V_{Rm} = V_R/m$, $V_{0m} = V_0/m$, $\Delta \rho_R^i = \rho_{R,I}^i - \rho_{R,F}^i$ and $\Delta \rho_S^i = \rho_{S,\text{Eq}}^i - \rho_{S,\text{Eq}}^{i-1}$, the Equation (1) can be

written as Equation (3).

$$\Delta n_i^{\text{ex}} = V_{\text{Rm}} \Delta \rho_{\text{R}}^i - V_{0\text{m}} \Delta \rho_{\text{S}}^i, \quad (3)$$

where V_{Rm} and $V_{0\text{m}}$ is specific volume of reference cell and specific void-volume of sample cell, respectively, cm^3/g ; $\Delta \rho_{\text{R}}^i$ and $\Delta \rho_{\text{S}}^i$ is density change of CO_2 in reference cell and sample cell, respectively, mmol/cm^3 .

If $x = V_0/V_{\text{R}}$, the Equation (2) can be written as Equation (4),

$$n_j^{\text{ex}} = V_{\text{Rm}} \left(\sum_{i=1}^j \Delta \rho_{\text{R}}^i - x \rho_{\text{S,Eq}}^j \right), \quad (4)$$

where x is a volume ratio of void of sample cell and reference cell.

b. The Density of CO₂

Although there are so many variables affecting the measured value of CO_2 Excess adsorption, the density of CO_2 is the root of the effect at high pressure. The CO_2 density (ρ) is a function of pressure (P) and temperature (T), which can be calculated by the Span and Wagner Equation of State (SW-EOS) [15]. The change of CO_2 density is used to explain the determination error of supercritical CO_2 sorption on coal with manometric apparatus at high pressure.

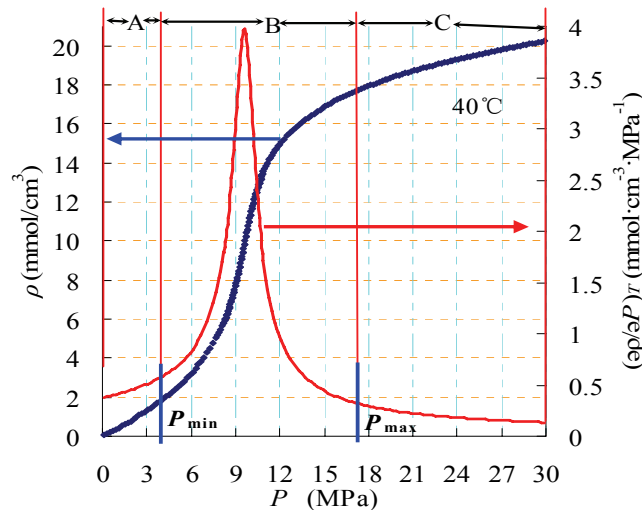


Figure1. The CO_2 density (ρ) and its change $[\partial \rho / \partial P]_T$ at 40°C , obtained from the SW-EOS

The CO₂ density (ρ) and its change value ($[\partial\rho/\partial P]_T$) at temperature of 40 °C and up to 30 MPa is shown in Figure 1. It can be seen from Figure 1 that the density-values increase with pressure increases, and the increment of density is different with pressure. The density smoothly increases with increasing pressure at pressure less than P_{\min} or higher than P_{\max} , and it sharply increases with the pressure at pressure between P_{\min} and P_{\max} .

c. The Density Change of CO₂

To theoretically investigate the CO₂ density change at a constant temperature, the derivative $[\partial\rho/\partial P]_T$ was obtained explicitly with the SW-EOS, as described as follows.

CO₂ density change at a constant temperature (T) is a partial derivative of the density (ρ) with respect to pressure (P) variable, i.e. $[\partial\rho/\partial P]_T$. Relation between CO₂ density and the reduced Helmholtz energy ϕ and its derivatives ϕ_δ is given in the Equation (5) [15].

$$\frac{P}{RT\rho} = 1 + \frac{\rho}{\rho_c} \phi_\delta^r \tag{5}$$

Rearranging Equation (5) gives

$$RT\rho + \frac{RT\rho^2}{\rho_c} \phi_\delta^r = P \tag{6}$$

From Equation (6), the partial derivative of ρ with respect to pressure (P) at a constant temperature (T) is expressed as

$$RT \left[\frac{\partial\rho}{\partial P} \right]_T + \frac{RT}{\rho_c} \left(2\rho\phi_\delta^r \left[\frac{\partial\rho}{\partial P} \right]_T + \rho^2 \left[\frac{\partial\phi_\delta^r}{\partial\rho} \right]_T \left[\frac{\partial\rho}{\partial P} \right]_T \right) = 1 \tag{7}$$

Rearranging Equation (7) gives

$$\left[\frac{\partial\rho}{\partial P} \right]_T = \frac{1}{RT(1 + 2\delta\phi_\delta^r + \delta^2\phi_{\delta\delta}^r)} \tag{8}$$

where $\delta = \rho/\rho_c$ is the reduced density, i.e. the density (ρ) normalised to the critical density ρ_c (10.627 mmol/cm³); ϕ^r is the residual part of the Helmholtz function, given by SW-EOS ; ϕ_δ^r is the derivative of ϕ^r ; $\tau = T_c/T$ is the inversed reduced temperature. The subscript c denotes the

critical values of both density and temperature. Here the Helmholtz energy is described as a function of density and temperature. The coefficients and exponents of Span and Wagner equation were provided in Table 31 in original paper [15]. The residual part of the dimensionless Helmholtz energy (ϕ^r) and its derivatives can be written as the following,

$$\phi_\delta^r = (\partial\phi^r / \partial\delta)_\tau, \phi_{\delta\delta}^r = (\partial^2\phi^r / \partial\delta^2)_\tau, \phi_\tau^r = (\partial\phi^r / \partial\tau)_\delta, \phi_{\tau\tau}^r = (\partial^2\phi^r / \partial\tau^2)_\delta \text{ and } \phi_{\delta\tau}^r = (\partial^2\phi^r / \partial\delta\partial\tau).$$

To investigate the effect of pressure change on CO₂ density change at a constant temperature, the $[\partial\rho/\partial P]_T$ was obtained with iterative calculation programmed with Visual FoxPro 6.0.

The $[\partial\rho/\partial P]_T$ value with pressure at the temperature of 35, 40, 50 and 60 °C and pressure of up to 30 MPa is shown in Figure 2. The $[\partial\rho/\partial P]_T$ increases first and then decreases with pressure increase. There is a maximum $[\partial\rho/\partial P]_T$ at a pressure, for example, 17.00 at 8.04 MPa, 6.61 at 8.84 MPa, 2.81 at 10.30 MPa and 1.76 mmol/cm³ at 11.70 MPa at 35, 40, 50, 60 °C, respectively. The maximum decreases, and its corresponding pressure increases with temperature increase.

It can be seen from Figures 1 and 2 that the density changes exhibit a three-stage tendency with the pressure increase. So, the density-change curve can be divided into three regions (i.e. A, B and C) based on CO₂ pressure and its corresponding density-change value ($[\partial\rho/\partial P]_T$) as seen in Figure 1. The region A at relatively low pressure and in region C at relatively high pressure are of a smaller $[\partial\rho/\partial P]_T$ value with the pressure change, and in the region B at high pressure is of a

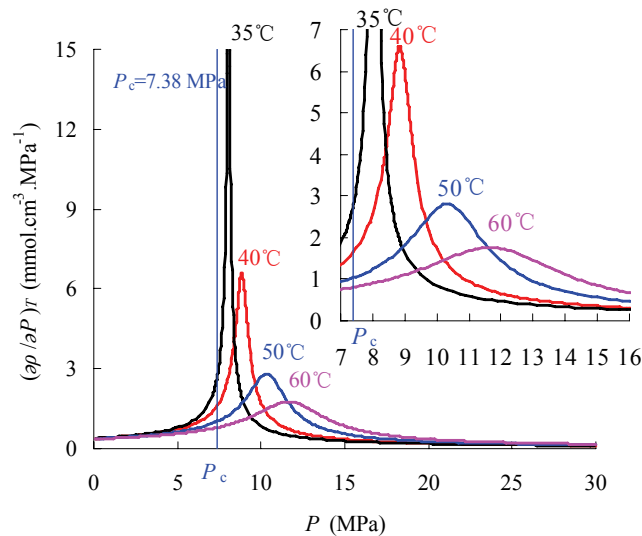


Figure 2. The comparison of CO₂ density change ($[\partial\rho/\partial P]_T$) with pressure at constant temperature, calculated with SW-EOS

greater $[\partial\rho/\partial P]_T$ value. The pressure ranges (P_{\max} - P_{\min}) in region B increase with temperature increase, as shown in Figure 2.

To express convenience in this paper, the pressure in region A, B and C is called low, medium and high pressure, respectively. The low pressure (P_{lo}) means the experiment pressure of lower than the critical pressure P_c (7.38 MPa) in the region A. The high pressure (P_{hi}) expresses the pressure with lower $[\partial\rho/\partial P]_T$ value in region C. The medium pressure means that of higher than P_c and lower than P_{hi} in region B, which depends on the temperature. For example, the P_{hi} is about 9, 10, 12 and 15 MPa at 35, 40, 50 and 60 °C, respectively.

III. SAMPLES AND EXPERIMENTAL METHOD

a. Samples and Experimental Apparatus

Three coal samples were selected to investigate the effect of pressure error on adsorption. The samples were crushed to pass through a 60-mesh sieve, and used for isotherm measurements as well as analysis of coal parameters. The -60 mesh coals were dried at 105 °C prior to adsorption analysis to avoid the effect of moisture in coal on CO₂ sorption determination. Proximate analysis and petrographic analysis for the coals are given in Table 1. Based on the analytical data as shown in Table 1, YN, NM and WY coal is brown coal, high-volatile bituminous and anthracite in rank, respectively.

Table 1: Analytical data of coal samples used for experiments

Coal	M_{ad} (%)	A_d (%)	V_{daf} (%)	$S_{t,d}$ (%)	R_{\max}^0 (%)	P_M^* (%)
YN	3.87	9.78	39.28	0.59	0.62	45
NM	9.01	7.81	36.97	0.35	0.89	89
WY	3.42	10.82	9.61	0.35	3.48	-

* P_M is transmittance for low rank coal.

Figure 3 shows a simplified scheme of the experimental set-up for manometric CO₂ adsorption experiments. The set-up consists of a stainless-steel sample cell (max. volume 50 cm³) and reference cell (max. volume 35 cm³), a set of needle valves, two of high-precision pressure sensors (max. pressure 25 MPa, with precision of 0.25 %) and two of micro Pt100 Platinum

resistance to determine the temperature of two cells. Temperature and pressure transmitters were used to convert the measuring signals into standard signal, which was recorded with a computer. A booster pump driven with compressed air is used to CO₂ pressurization. The volume of the reference cell (V_R) and void volume of sample cell (V_0) were determined by helium expansion.

The two cells, needle valves and pressure sensors are kept in a temperature-controlled water bath, the temperature of which is constant to ± 0.1 K of the set-point. The feed gas is stored in a gas cylinder for pure CO₂ (99.99 %).

Pressure sensor accuracy is typically expressed as percent of full scale (% FS). An error coefficient expressed as % FS can be changed to a unit of pressure by multiplying by the range, ($P_{\max} - P_{\min}$), and dividing by 100. In this study, pressures are measured using the pressure sensors HM10 manufactured by Nanjing Helm Sci-tech Co., Ltd. The overall accuracy is 0.25% FS, and

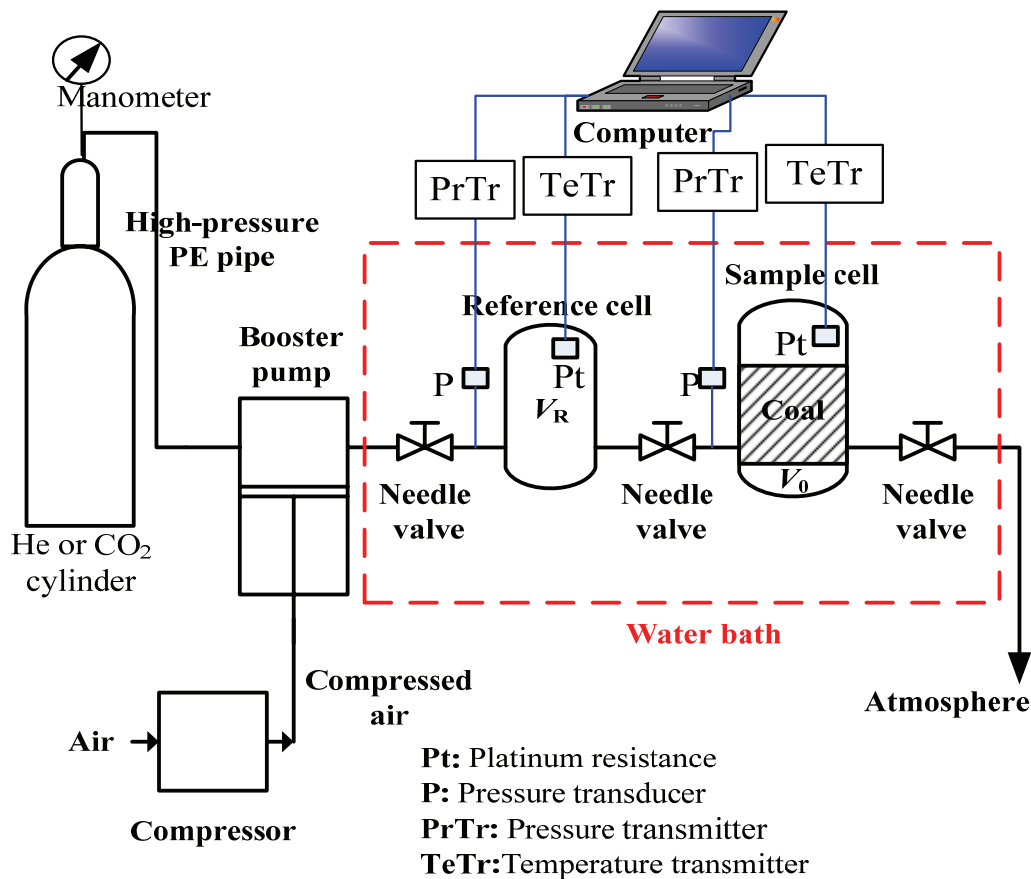


Figure 3. Simplified scheme of the experimental setup for CO₂ sorption measurement

measuring range is 0-25 MPa, so the error value of the pressure is 0.0625 MPa. The pressure change (ΔP) of 0.05 MPa is used to investigate the effect of pressure-sensor error in two cells on adsorption.

Although the manometric technique was accepted to determine the CO₂ sorption on coal by many investigators, only the few provide the accuracy of the pressure sensors, such as less than 0.1 bar [16], 0.08% FS [17], $\pm 0.36\%$ FS [18], and 0.25% FS [19].

b. Experimental Procedure

Manometric CO₂ sorption experiments on three coals were conducted in a programmed mode at temperatures of 40 °C and pressures up to 20 MPa. An m g (about 10 g) portion of the powdered and dried coal samples were placed into the sample cell, which was then connected into with set-up and tested leaks. At the beginning of the experiment, all cells were evacuated using vacuum pump to establish a defined starting condition. Before the start of an adsorption experiment, the void volume of two cells was determined volumetrically using He and calculated with standard Boyle's law methodology.

The experimental parameters for CO₂ adsorption are given in table 2.

Table 2: Experimental parameters for CO₂ adsorption

Coal	T (°C)	Volume (cm ³)		m (g)	Specific volume (cm ³ /g)		V_R/V_0
		V_R	V_0		V_{Rm}	V_{0m}	
YN	40	35.4121	40.2345	10.3568	0.342	0.389	0.880
NM	40	35.3862	39.1307	13.4367	0.263	0.291	0.904
WY	40	35.3929	42.7789	9.7794	0.362	0.438	0.827

IV. RESULTS AND DISCUSSION

a. Base

In order to construct an adsorption isotherm, the following conditions must be met: (1) the equilibrium pressure in the sample cell must incrementally increase, $P_{S,Eq}^i > P_{S,Eq}^{i-1}$; (2) A portion of CO₂ is transferred from the reference cell to the sample cell, at this point, $P_{R,I}^i > P_{R,F}^i$. The CO₂

density increases with pressure increase, just shown in Figure 1. Consequently, the CO₂ density values in two cells increase with equilibrium pressure increasing in the sample cell, $\rho_{R,I}^i > \rho_{R,F}^i$ and $\rho_{S,Eq}^i > \rho_{S,Eq}^{i-1}$.

The Excess sorption of CO₂ can be calculated from Equations (1) and (2). The incremental Excess-adsorption (Δn_i^{ex}) is zero or positive if no adsorbed CO₂ is desorbed from coal as CO₂ expansion from reference cell into sample cell.

From Equation (3), the relation between the CO₂ 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_0), involves three case, i.e. (1) $\Delta\rho_S^i/\Delta\rho_R^i = V_R/V_0$, (2) $\Delta\rho_S^i/\Delta\rho_R^i < V_R/V_0$ and (3) $\Delta\rho_S^i/\Delta\rho_R^i > V_R/V_0$ in case of zero, positive and negative adsorption increment (Δn_i^{ex}), respectively. The V_R/V_0 value is constant for a manometric setup and known coal sample. The V_R/V_0 values were between 0.8 to 0.9 from Table 2. A smaller volume of reference cell or lower V_R/V_0 value is not favorable to raise the pressure in the sample cell.

b. The Density Change

Figure 4 shows CO₂ density changes ($[\partial\rho/\partial P]_T$) at the pressure of $P_{R,I}^i$, $P_{R,F}^i$, $P_{S,Eq}^{i-1}$ and $P_{S,Eq}^i$, obtained during CO₂ sorption determination in this study. It should be noted that the x axis in Figure 4 expresses the equilibrium pressure ($P_{S,Eq}^i$) of the sample cell for i^{th} step, and the points expresses the $[\partial\rho/\partial P]_T$ values of the initial and final pressures in the reference cell ($P_{R,I}^i$ and $P_{R,F}^i$), the equilibrium pressure of the sample cell for $(i-1)^{\text{th}}$ step ($P_{S,Eq}^{i-1}$) and i^{th} step ($P_{S,Eq}^i$). The serial numbers in the Figure 4 indicate CO₂ expansion step.

Initial pressures in the reference cell ($P_{R,I}^i$) may controlled with the CO₂ booster-pump. From the Figure 4, the $[\partial\rho/\partial P]_T$ values are from 0.16 to 1.06, 0.19 to 1.03 and 0.16 to 1.01 mmol/(cm³·MPa) for YN, NM and WY coal at $P_{R,I}^i$, respectively. Based on the Table 2 and the above $[\partial\rho/\partial P]_T$ values, the error of sorption increment is less than 0.002 mmol/g with pressure-sensor accuracy of 0.05 MPa.

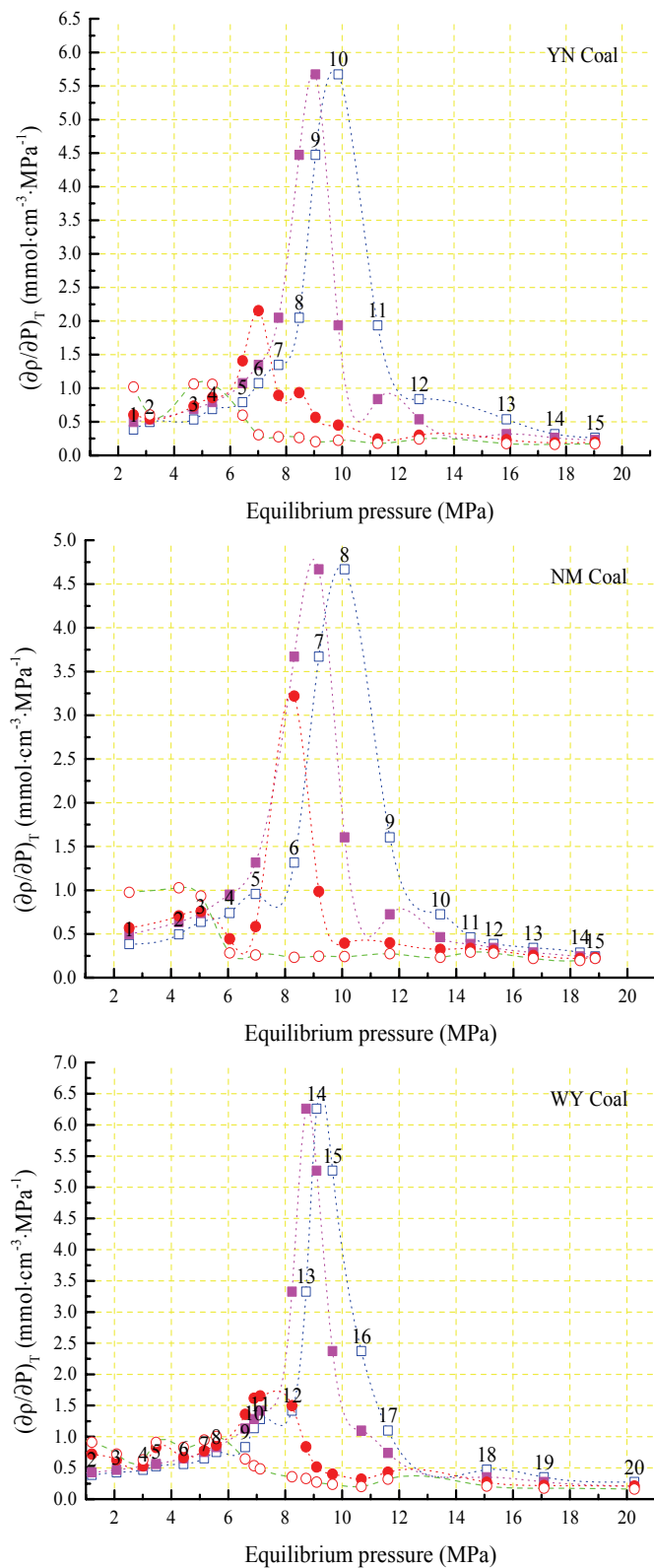


Figure 4. CO₂ density changes at its corresponding pressure ($\square: P_{S,Eq}^{i-1}$; $\diamond: P_{S,Eq}^i$; $\bullet: P_{R,F}^i$; $\circ: P_{R,I}^i$) at 40 °C

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The final pressures in the reference cell ($P_{R,F}^i$) can also be controlled by regulating the CO₂ quality expanded into sample cell with needle valve between the two cells. From the Figure 4, the $[\partial\rho/\partial P_{R,F}^i]_T$ values for the reference cell are from 0.19 to 2.16, 0.20 to 3.22 and 0.21 to 1.66 mmol/(cm³·MPa) for YN, NM and WY coal at $P_{R,F}^i$, respectively. Based on the Table 2 and the above $[\partial\rho/\partial P_{R,F}^i]_T$ values, the error of sorption increment is less than 0.004 mmol/g.

The equilibrium pressures of the sample cell for ($i-1$)th step ($P_{S,Eq}^{i-1}$) and i th step ($P_{S,Eq}^i$) are dependent on the CO₂ quality expanded from the reference cell and sorption amount on coal. From the Figure 4, most of the $[\partial\rho/\partial P_{S,Eq}^i]_T$ value is less than 2.0 mmol/(cm³·MPa), there are 3, 2 and 4 pressure points' $[\partial\rho/\partial P_{S,Eq}^i]_T$ values greater than 2 mmol/(cm³·MPa), and the maximum $[\partial\rho/\partial P_{S,Eq}^i]_T$ is 5.67, 4.67, 6.26 mmol/(cm³·MPa) for YN, NM and WY coal, respectively. Based on the Table 2 and the above $[\partial\rho/\partial P_{R,F}^i]_T$ values, the error of sorption increment is 0.11, 0.068 and 0.14 mmol/g. Also, the same sorption increment error may be caused by the error of the equilibrium pressures ($P_{S,Eq}^{i-1}$) for ($i-1$)th step. So, the increment error is 0.22, 0.13 and 0.28 mmol/g for YN, NM and WY coal, respectively, caused by pressure error in the sample cell.

Table 3: CO₂ density change and volume ratio of two cells as no sorption increment on coal at 40 °C

i	P_i (MPa)	Density, ρ (mmol/cm ³)		Volume ratio	
		ρ	$\rho_{i+1}-\rho_i$	V_R/V_0	$\sum_{i=1}^n [V_R/V_0]_i$
0	6	3.39	-	-	-
1	7	4.50	1.11	0.25	0.25
2	8	6.32	1.82	0.41	0.66
3	8.5	8.04	1.72	0.39	1.05
4	9	11.03	2.99	0.67	1.72
5	10	14.29	3.26	0.73	2.45
6	11	15.53	1.24	0.28	2.73
7	25	19.99	4.45	-	-

The characteristics of CO₂ density change determine that the equilibrium pressures of the sample cell in region B (a greater $[\partial\rho/\partial P]_T$) is probably inevitable, which means greater error of sorption measurement. The CO₂ density changes in reference cell in region C and the change in sample cell in region B are used to explain the inevitability. The $P_{R,I}^i$ and $P_{R,F}^i$ being 25 and 11 MPa, $P_{S,Eq}^{i-1}$ and $P_{S,Eq}^i$ being from 6 to 11 MPa are used to calculate the density change in two cells in case of no sorption increment on coal. The table 3 gives the density (ρ) and its change ($\rho_{i+1}-\rho_i$) at a pressure (P_i), the volume ratio (V_R/V_0) and its accumulative total ($\sum_{i=1}^n [V_R/V_0]_i$). So, the V_R/V_0 is the volume ratio of two cell as no sorption on coal and at the pressure decrease from 25 MPa to 11 MPa in the reference cell and increase from P_i to P_{i+1} in the sample cell, and $\sum_{i=1}^n [V_R/V_0]_i$ is the volume ratio at the pressure increase from 6 MPa to P_{i+1} in the sample cell.

From Table 3, the volume ratio is 0.73 at equilibrium pressure of 9 MPa increasing to 10 MPa, which is easily conducted. But, the pressure in the sample cell increase from 6 MPa to 11 MPa is difficult to be conducted as the volume ratio of 2.73. Under this sorption manometric set-up conditions, the equilibrium pressures with a greater $[\partial\rho/\partial P]_T$ value in the sample cell are inevitable.

In the practical measurement of sorption, a smaller void volume in sample cell means a greater measurement error of this volume with He expansion method. Temperature increases or decreases in the two cells as a result of the Joule-Thompson effect [15] during CO₂ expansion procedure. The determination of CO₂ sorption isotherm is at a constant temperature, and the CO₂ temperatures in two cells must be reached the temperature of the water bath. It is difficult to establish the thermal balance of CO₂ in the reference cell with a greater volume. Temperature measurement error also results in a greater error of sorption measurement. So, the equilibrium pressures with a greater $[\partial\rho/\partial P]_T$ value in the sample cell are inevitable.

c. Error of Sorption

c.i Basis

The observed pressure parameter in the experiments has random and systematic errors [20, 21]. The systematic error of the pressure sensor is defined as the accuracy of the sensor [22]. Based on error propagation, the expected error limit of Excess sorption increment at i^{th} expansion-step due

to the sensor error is calculated with Equation (9), used to estimate CO₂ sorption error by some researcher [19].

Equation (10) can be used to determine the error limit of Excess total sorption at j^{th} step.

$$d\Delta n_i^{\text{ex}} = \frac{\left[\left(\frac{\partial \rho}{\partial P_{R,I}^i} \right)_T \Delta P_{R,I}^i + \left(\frac{\partial \rho}{\partial P_{R,F}^i} \right)_T \Delta P_{R,F}^i \right] V_R + \left[\left(\frac{\partial \rho}{\partial P_{S,\text{Eq}}^{i-1}} \right)_T \Delta P_{S,\text{Eq}}^{i-1} + \left(\frac{\partial \rho}{\partial P_{S,\text{Eq}}^i} \right)_T \Delta P_{S,\text{Eq}}^i \right] V_0}{m} \quad (9)$$

$$dn_j^{\text{ex}} = d\Delta n_1^{\text{ex}} + d\Delta n_2^{\text{ex}} + \dots + d\Delta n_i^{\text{ex}} + \dots + d\Delta n_j^{\text{ex}} \quad (10)$$

The expected standard error [13, 23] of sorption increment at i^{th} step is calculated with (11), and the standard error of total sorption is calculated with Equation (12). The standard error has been widely used to calculate the sorption error on coal [10, 13, 24].

$$d\Delta n_i^{\text{ex}} = \frac{\sqrt{\left[\left(\frac{\partial \rho}{\partial P_{R,I}^i} \right)_T \Delta P_{R,I}^i V_R \right]^2 + \left[\left(\frac{\partial \rho}{\partial P_{R,F}^i} \right)_T \Delta P_{R,F}^i V_R \right]^2 + \left[\left(\frac{\partial \rho}{\partial P_{S,\text{Eq}}^{i-1}} \right)_T \Delta P_{S,\text{Eq}}^{i-1} V_S \right]^2 + \left[\left(\frac{\partial \rho}{\partial P_{S,\text{Eq}}^i} \right)_T \Delta P_{S,\text{Eq}}^i V_S \right]^2}}{m} \quad (11)$$

$$dn_j^{\text{ex}} = \sqrt{\left(d\Delta n_1^{\text{ex}} \right)^2 + \left(d\Delta n_2^{\text{ex}} \right)^2 + \dots + \left(d\Delta n_i^{\text{ex}} \right)^2 + \dots + \left(d\Delta n_j^{\text{ex}} \right)^2} \quad (12)$$

The density-change value was calculated with $[\partial \rho / \partial P]_T$ (Equation (8)) or the actual difference of density at pressure (P) and ($P + \Delta P$) with SW-EOS. The change is used to calculate the error of sorption and its increment with Equations (9)-(12). The former is called derivative method, and the latter is called actual method in this paper.

c.ii Derivative method

Firstly, the derivative method is used to estimate sorption error at pressure error of 0.05 MPa. The Excess CO₂ sorption increment, total sorption isotherms and their errors at 40 °C on three dried-coals are shown in Figure 5. The Figure 5 displays error limit (calculated with Equations (9) and (10)) with fill area plots, standard error (calculated with Equations (11) and (12)) with error bar, and sorption increment and total sorption with dot-line. The serial number in the Figure 5 indicate CO₂ expansion step just as shown in the Figure 3.

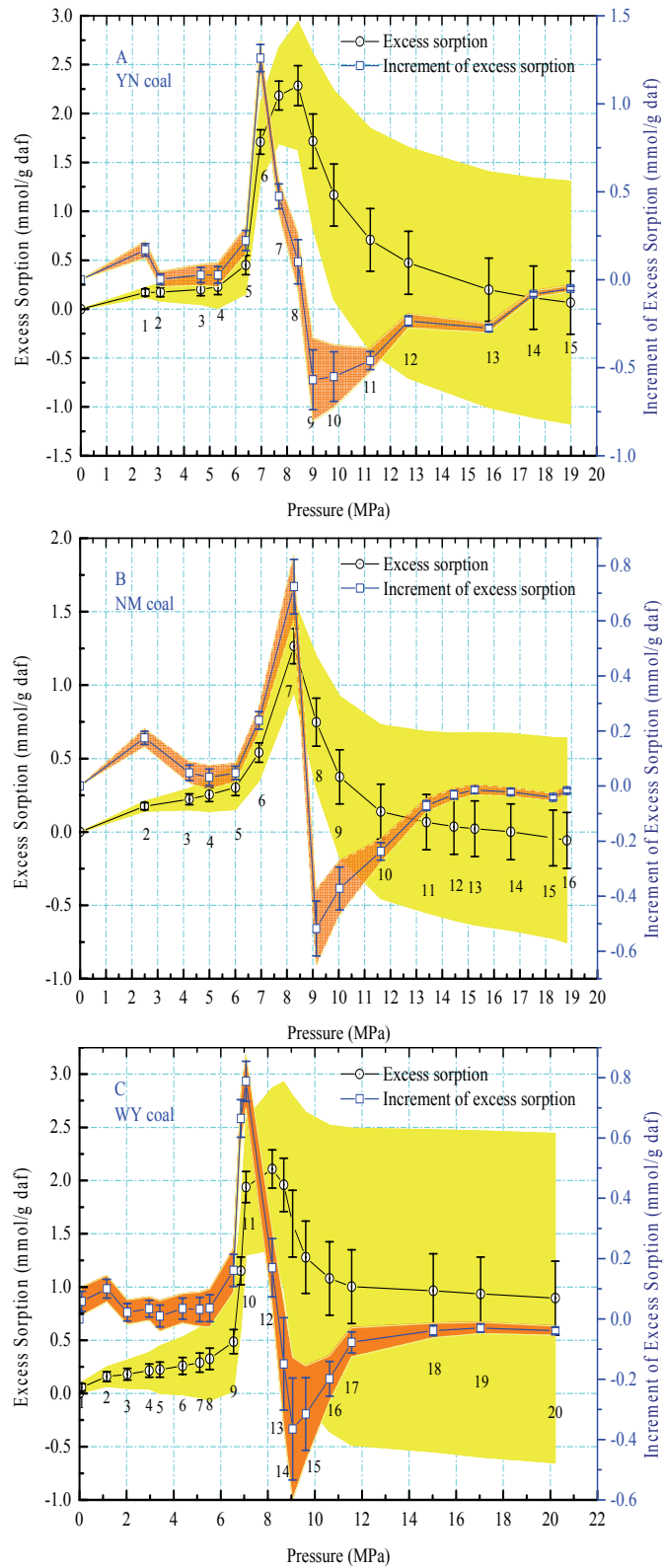


Figure 5. The Excess sorption increment and its isotherms (dot-line), error limit (fill area plot) and standard (error bar) errors of sorption increment and total sorption calculated with $[\partial\rho/\partial P]_T$

With the derivative method, the error limit of increment calculated with Equation (9) is greater than the standard error of increment calculated with Equation (11), especially, at pressure of 8-10 MPa. With pressure increase, the error limit of the increment increases to a maximum and then decrease. The maximum appears at a pressure range of 8-10 MPa, being consistent with the maximum $[\partial\rho/\partial P]_T$ is 6.25 mmol/(cm³·MPa) at 40 °C and 8.95 MPa. The pressure range is at medium pressure as mentioned in Section 2.3. The increment error is very lower at lower than 8 MPa (low pressure) and higher than 10 MPa (high pressure). The maximum error of sorption increment appears at a pressure with negative increment-sorption. The negative increment at i^{th} step indicates the maximum sorption at $(i-1)^{\text{th}}$ step. The reason why the negative increment or maximum sorption is at a maximum increment-error should be studied in the future.

The error limit of sorption calculated with Equations (9) and (10) is an extreme value, plotted with fill area in Figure 5. The error limit is very greater, accounting for 54.32%, 55.05% and 73.35% of maximum adsorption for YN, NM and WY coal, respectively. The negative sorption will appear for YN, NM and WY coal as negative error limit, and the shape of sorption isotherm will change for WY coal as positive error-limit.

The standard error calculated with Equations (11) and (12), and plotted with error bar in Figure 5, accounts for 14.16%, 15.04% and 16.49% of maximum adsorption for YN, NM and WY coal, respectively. Although the standard error is smaller than error limit, the negative sorption still appears for YN coal as negative standard error.

c.iii Actual method

It is worth suspecting that such a larger error of sorption and its increment is calculated with derivative method ($[\partial\rho/\partial P]_T$) at a pressure in region B. The difference between $0.05[\partial\rho/\partial P]_T$ and the actual density change ($\Delta\rho$) is shown in Figure 6. Where $\Delta\rho=(\rho_P - \rho_{P-0.05})$ or $\Delta\rho=(\rho_{P+0.05} - \rho_P)$, and $\rho_{P-0.05}$, ρ_P and $\rho_{P+0.05}$ is CO₂ density at a pressure ($P-0.05$), P and ($P+0.05$), respectively. From Figure 5, The $[\partial\rho/\partial P]_T$ value is higher than density-change value ($\Delta\rho$) as the pressure (P) is higher than the pressure (P_{max}) corresponding with maximum $[\partial\rho/\partial P]_T$, and lower than $\Delta\rho$ as $P > P_{\text{max}}$. Because of the error calculation of sorption increment with the absolute value (Equation (9)) or square of density change (Equation (11)), so the sorption error calculated with $[\partial\rho/\partial P]_T$ (derivative method) should higher than that with the actual density change (actual method).

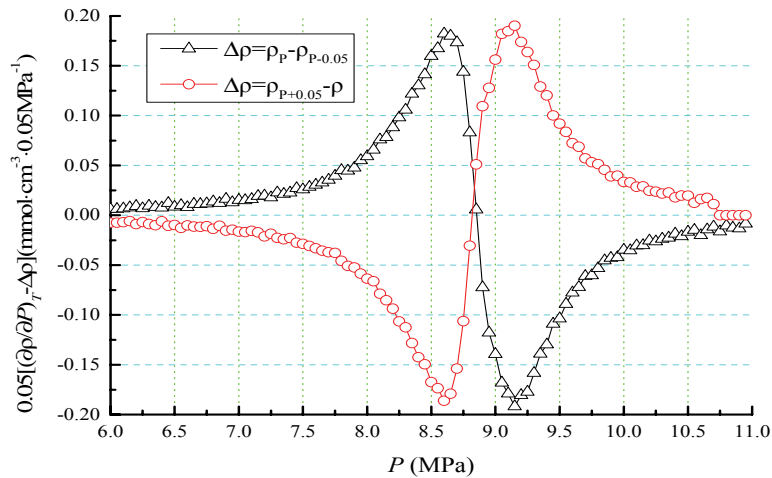


Figure 6. The difference between $0.05[\partial\rho/\partial P]_T$ and $\Delta\rho$

The actual method is used to calculate the errors of sorption and its increment for pressure error of 0.05 MPa. The CO₂ density at pressure of $(P-0.05)$, P and $(P+0.05)$ are calculated with SW-EOS, respectively, where P is a pressure of $P_{R,I}^i$, $P_{R,F}^i$, $P_{S,Eq}^i$ and $P_{S,Eq}^{i-1}$. So, 12 density data are obtained with SW-EOS, and 12 Excess-sorption-increment data are obtained with Equation (1) and these density data, for each CO₂-expansion step. The $(\Delta n_{i,max}^{ex} - \Delta n_i^{ex})$ and $(\Delta n_i^{ex} - \Delta n_{i,min}^{ex})$ is used as a positive error and negative error, respectively, where $\Delta n_{i,max}^{ex}$ and $\Delta n_{i,min}^{ex}$ is the maximum value, minimum value among these 12 sorption-increments, respectively; Δn_i^{ex} is the sorption increment at the pressure of P , i.e., pressure error being zero.

Figure 7 shows the error limit and standard errors of increment and total sorption calculated with the actual density, and the sorption isotherm of CO₂ on coals. From Figure 7, all errors calculated with the actual density change are significantly lower than that with $[\partial\rho/\partial P]_T$. There is a difference of the pressure responding with a maximum increment-error obtained with the actual method and derivative method. The maximum error of increment appears at about from 8 to 10 MPa, not as the derivative method at about 9 MPa.

The maximum error of total sorption accounts for 30.07%, 32.25% and 32.15% of maximum adsorption for YN, NM and WY coal, respectively. The negative sorption still appears for YN with the maximum error obtained with actual method, just as derivative method. The standard error accounts for 11.29%, 14.78% and 11.14% of maximum adsorption for YN, NM and WY coal, respectively. The negative sorption still appears for YN coal with actual method and standard error.

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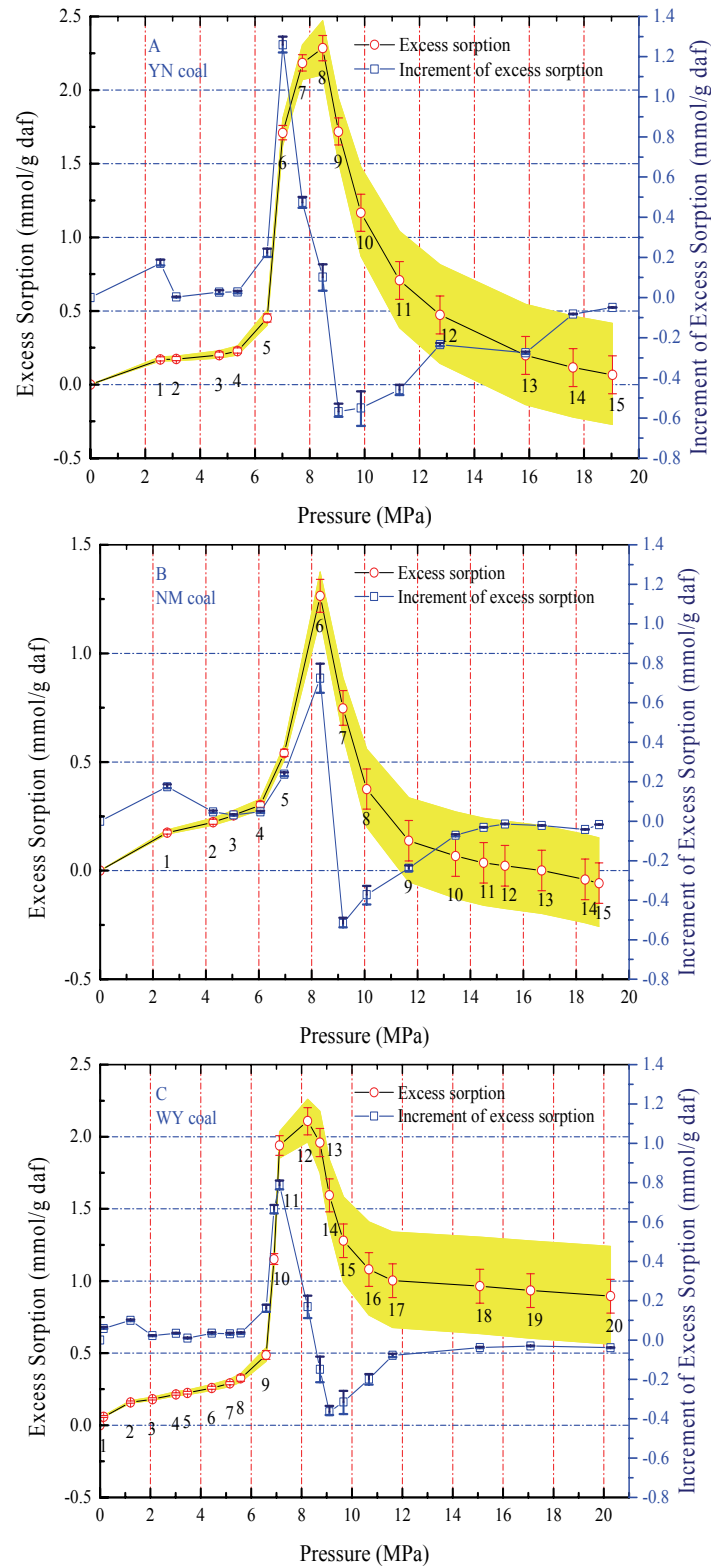


Figure 7. The Excess sorption increment and its isotherms (dot-line), error limit (fill area plot) and standard (error bar) errors of sorption increment and total sorption calculated with actual density method

d. *The Reason Why the Sorption Measurement at a Higher Temperature*

Some works have been carried on CO₂ sorption experiment on coal at high pressure, but the experimental temperature is obviously higher than a critical temperature of CO₂ ($T_c=30.98$ °C), such as 40 °C [25], 45 °C [8, 26], 55 °C [4, 19, 27], 60 °C [25] and 80 °C [25]. To avoid condensation of CO₂ in the sorption apparatus at a lower temperature is a reason why the sorption measurement on coal at a higher temperature, the greater $[\partial\rho/\partial P]_T$ value at a lower temperature is a key reason for this. The greater $[\partial\rho/\partial P]_T$ value may cause bad agreement of sorption isotherms among different experimental round for a same coal sample.

From Figure 2, the $[\partial\rho/\partial P]_T$ or CO₂ density-change value caused by pressure-change increases with temperature decrease. So, the measurement error of sorption caused by accuracy of the pressure-sensor will increase with experimental temperature decrease.

VI. CONCLUSIONS

- (1) The characteristic of CO₂ density-change determines pressure error has different effects on measured error of CO₂ sorption isotherm on coal in the different stage of pressure. The pressure sensor accuracy has significant influence on Excess sorption increment of CO₂ on coal with manometric equipment in medium pressure (7-12 MPa), and little influence on the increment in low and high pressure, which depend on the experimental temperature. The accuracy has significant influence on CO₂ Excess-sorption isotherm at medium and high pressure as the propagation of increment error.
- (2) The equilibrium medium-pressures with a greater CO₂ density-change with pressure at a constant temperature ($[\partial\rho/\partial P]_T$) in the sample cell are probably inevitable, as a result of a finite volume ratio of the reference volume to the void-volume in the sample cell, which means a greater error of sorption.
- (3) The error limit of sorption-increment calculated with $[\partial\rho/\partial P]_T$ of derivative method is significantly larger, and the error calculated with the CO₂-density of actual method is proper. The standard error of sorption obtained with the actual method is more suitable for expression of the effect of pressure sensor accuracy on CO₂ isotherm on coal.
- (4) A higher temperature is a key experimental parameter in manometric CO₂ sorption

experiments on coal, just as accept by many investigators. A lower experiment-temperature will reduce a greater sorption error caused by pressure sensor accuracy.

- (5) The pressure sensor accuracy may result in the less reproducibility and repeatability of CO₂ adsorption on coals at high pressure, and negative sorption increment and even negative adsorption. Especially, the extreme error of sorption increment obtained density-change calculated with $[\partial\rho/\partial P]_T$ in derivative method may change the shape of Excess sorption of CO₂ on coal.

VII. ACKNOWLEDGEMENTS

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