Experimental determination of deviation factor of natural gas in natural gas reservoir with high CO_2 content

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Abstract. The deviation factor of natural gas is a coefficient to quantitatively describe the deviation degree between real gas (natural gas) and ideal gas. Generally, the deviation factor of natural gas is measured in PVT cell without considering porous media. However, when natural gas is in underground porous media reservoir, due to the adsorption of porous media, the deviation factor of natural gas in porous media deviates from that measured in conventional PVT cell. Moreover, compared with other gases, CO_2 has stronger adsorption capacity. Therefore, in porous media, the deviation factor of natural gas considering the adsorption of porous media is quite different from that measured in conventional PVT cell. In this paper, simulating the isothermal mining conditions in gas reservoir,the deviation factor of natural gas with different CO_2 content considering the influence of porous media under different pressure isothermal conditions is studied by using the test of designed sand filled long slim tube in series. And under the same conditions, the deviation factor is compared with that of conventional PVT. The experimental results show that under the same conditions, due to the adsorption of porous media, the deviation factor measured in porous media is smaller than that measured by PVT cell without considering porous media.

1 Introduction

In recent years, CO_2 rich natural gas reservoirs have been found one after another, and the variation range of CO_2 content can reach 5% ~ 98% [1]. Natural gas is rich in CO_2, which reduces the quality of natural gas. However, after separation, CO_2 can be used for miscible flooding and immiscible flooding of gas injection in oil fields, which is conducive to the production of ultra-low permeability undeveloped reserves, the enhancement of oil recovery of used petroleum geological reserves, and the realization of greenhouse gas storage and resource utilization.

However, different CO_2 content in natural gas results in different deviation factor of natural gas[2]. The deviation factor of natural gas is an essential parameter in many petroleum calculations. There are four methods to obtain the deviation factor of natural gas, namely: experimental test method[3-5], state equation method[6-9], corresponding state correlation and empirical formula method[10-14]. The experimental test method is the most accurate of these methods. Although many scholars have studied and measured the deviation factor of natural gas under different experimental conditions and circumstances for many years, the experimental measurement of the deviation factor of natural gas with high CO_2 content in porous media is rarely studied. One is to test the deviation factor of natural gas, which does not consider the different CO_2 content in porous media, through the RUSKA-PVT instrument manufactured by fluke company of the United States. The second is to measure the deviation factor of natural gas with different CO_2 content in porous media in the designed sand filled long slim tube in series.

2 Experimental study

2.1. Experimental principle and device

2.1.1. Experimental device and principle in porous medium

The experimental test of the deviation factor of natural gas with high CO_2 content in porous media is carried out in sand filled long slim tube in series. The parameters of the thin tube are shown in Table 1, and the experimental flow chart is shown in Figure 3.The sand filled long slim tube in series is located in the constant temperature oven shown in Figure 1. In order to ensure the temperature of the experiment, the maximum working temperature of the oven is 180℃, and the temperature resolution is 0.1℃.The pressure required for the experiment is provided by RUSKA high-precision displacement pump shown in Figure 2. The working pressure range of RUSKA high-precision displacement pump is 0 ~ 10000 Psia, and the

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pressure resolution is 1 Psia. The experimental test is based on the principle of gas expansion, i.e. Boyle's law. In order to ensure the accuracy of the experimental test and avoid the influence of temperature and pressure on the pore volume of the slim tube, the pore volume of the slim tube was tested under the experimental temperature and pressure.That is to say, the volume of gas in the standard chamber (slim tube 1) is known, and isothermal expansion is made to the unknown chamber (slim tube 2, slim tube 3, slim tube 4, slim tube 5) under the determined pressure. After the state is stable, the final equilibrium pressure can be determined.The equilibrium pressure depends on the volume of the unknown chamber. The volume of the unknown chamber is obtained from formula (1) and formula (2) :

The volume of the No.1 unknown chamber

$$V_1 = \frac{V_k + (P_k - P_1)}{P_1} \quad (1)$$

The volume of the No.i unknown chamber:

$$V_i = \frac{(V_k + \sum_{i=2}^{n} V_{i-1})(P_{i-1} - P_i)}{P_i} \quad (i=2,3, \ldots n) \quad (2)$$

Where, P_1—Equilibrium pressure of slim tube 1 (the standard chamber) and slim tube 2 (the unknown chamber 1) in series , MPa. V_1—The pore volume of slim tube 2 (the unknown chamber 1), ml. P_k— The pressure of slim tube 1 (the standard chamber), MPa. V_k—The pore volume of slim tube 1 (the standard chamber), ml. V_i—The pore volume of slim tube i+1 (the unknown chamber i), ml. V_{i-1}—The pore volume of slim tube i (the unknown chamber i~1), ml.$P_{i\sim1}$—Equilibrium pressure of slim tube i (the unknown chamber i~1) connected with slim tube 1 (the standard chamber), MPa. P_i—Equilibrium pressure of slim tube i+1 (the unknown chamber i) connected with slim tube 1 (the standard chamber), MPa.

After the pore volume of standard chamber (slim tube 1) and each unknown chamber under experimental temperature and pressure is known, the deviation factor of natural gas with high CO_2 content in porous media under experimental temperature and pressure is obtained by formula (3).

$$Z_{i+1} = \frac{P_{i+1} V_{i+1} Z_i}{P_i V_i} \quad (i=1,2, \ldots n) \quad (3)$$

Where, P_i—The pressure of the No.i slim tube, MPa. P_{i+1}—The pressure of slim tube i+1 connected with slim tube i, MPa. V_i—The pore volume of the No.i slim tube, ml. V_{i+1}—The volume of slim tube i+1 connected with slim tube i,ml. Z_i—Deviation factor of gas in the No. i slim tube. Z_{i+1}—Deviation factor under the pressure of slim tube i+1 connected with slim tube i.

Table 1. The parameters of the thin tube

Diameter (mm)	Length (cm)	Pore volume (cm^3)	Porosity (%)	Permeability (μm^2)	Specific surface area (cm^2/cm^3)
4.4	1900	91.137	31.56	8.1	224.29
4.4	500	23.224	31.56	7.7	219.20
4.4	600	28.731	30.56	8.4	219.68
4.4	1300	61.389	31.50	7.1	234.01
4.4	1750	83.439	31.07	9.3	207.44

Figure 1. HYCAL constant temperature oven

Figure 2. RUSKA high-precision displacement pump

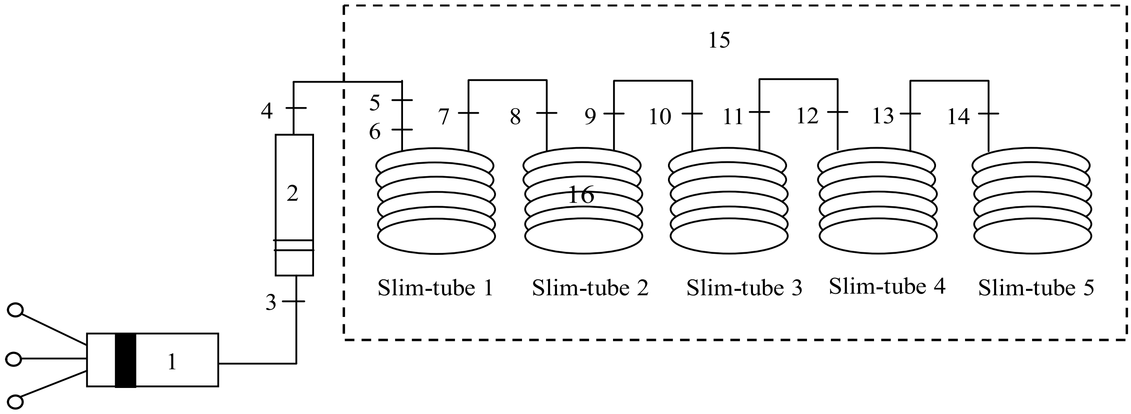


Figure 3. Flow chart of experimental device for deviation factor of natural gas with high CO_2 content in porous media
1.Displacement pump 2.Injected gas 3.Intermediate container inlet valve 4.Intermediate container outlet valve 5.No.1 slim tube inlet valve 6.No.1 slim tube inlet pressure gauge valve 7.No.1 slim tube outlet valve 8.No.2 slim tube inlet valve 9.No.2 slim tube outlet valve 10.No.3 slim tube inlet valve 11.No.3 slim tube outlet valve 12.No.4 slim tube inlet valve 13.No.4 slim tube outlet valve 14.No.5 slim tube inlet valve 15.Constant temperature air bath 16. Slim tube

2.1.2. Experimental device and principle without considering porous medium

RUSKA2370-601A pumpless PVT instrument is used to measure the deviation factor of natural gas without considering high CO_2 content in porous media. Performance index of RUSKA2370-601A pumpless PVT instrument: The maximum working pressure is 70 MPa, the pressure resolution is 1 Psi, the maximum working temperature is 200 ℃, and the temperature resolution is 0.1 ℃. The experimental device and flow chart are shown in Fig. 4 and Fig. 5.

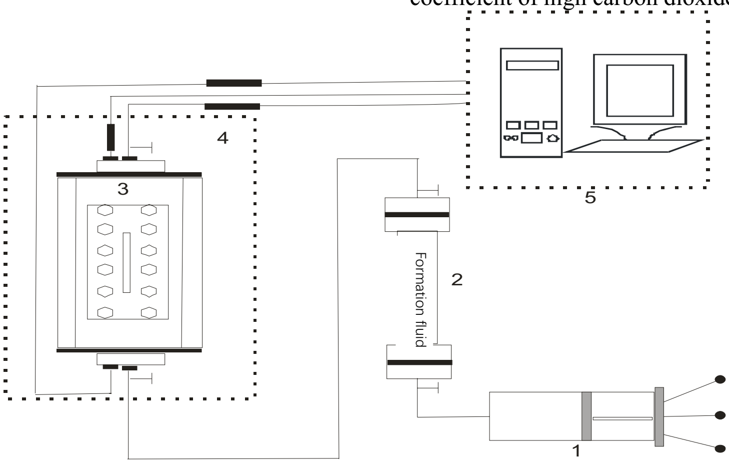
The experimental device includes: PVT test unit (about 350ml), constant temperature air bath, gas meter, flash separator, gas chromatographic instrument, ground separator and automatic pump.

The method to measure the deviation factor of natural gas without considering porous media is that firstly the volume of natural gas is measured under the constant temperature and pressure required by the experiment , then the volume of natural gas is measured under the room temperature and pressure, and finally the deviation factor is calculated by the gas state equation. The calculation formula goes as below[20]:

$$Z = \frac{P\Delta V T_s}{(P_s - P_w) V_s T} \tag{4}$$

Where, P—Experimental pressure, MPa. P_s—room pressure, MPa. P_w—Wet gas meter is the saturated vapor pressure of water at room temperature, dry gas meter is 0, MPa. T—Experimental temperature,K. T_s—room temperature, K. $\triangle V$—Volume of gas discharged from PVT cell, ml. V_s—Volume of gas discharged at room temperature and pressure, ml. Z—Deviation factor of natural gas.

Figure4. The experiment device diagram for the deviation coefficient of high carbon dioxide gas without porous media



1.Automatic pump 2.Intermediate container 3.PVT Test unit 4.Air washing in constant temperature 5.Computer
Figure5. The flow diagram of the experimental device for the deviation coefficient of high carbon dioxide gas without porous media

2.2 Experimental Process

2.2.1 Experimental Process Considering Porous Media

(1) Connect the pipelines according to the experimental process in Figure3;

(2) Cleaning、drying and vacuuming all pipes and pipelines, And measuring pore volume of the slim tube 1 (standard room) and connecting pipeline with N_2 under experimental temperature and pressure (80℃, 42.34 MPa);

(3) Vacuuming the thin pipe 1 (standard room) and connecting pipeline again;

(4) Natural gas with a certain CO_2 concentration was injected into the first tubule by the pump, and it was stabilized for a period of time at 80℃ and 42.34 MPa, so that the first tubule was fully saturated, that is, the position and pressure of the pump remained unchanged. Then, the gas is released into the RUSKA-PVT instrument to test the deviation coefficient of the first fine tubule natural gas ;

(5) Empty the first tubule and pipeline, inject a certain CO_2 concentration of natural gas into the first tubule with a pump, stable for a period of time at 80℃, 42.34 MPa, so that the first tubule is fully saturated, that is, when the position and pressure of the pump remain unchanged, close the inlet valve of the first tubule, connect the first and second tubules , and record the equilibrium pressure of the two tubules when the pressure shown by the pressure sensor is basically unchanged ;

(6) Connect the 1st, 2nd and 3rd tubules, and record the equilibrium pressure of the 3 tubules when the pressure displayed by the pressure sensor is basically unchanged ;

(7) Connect the 1st, 2nd, 3rd and 4th fine tubules, when the pressure displayed by the pressure sensor is basically unchanged, the equilibrium pressure of the 4 fine tubules is recorded;

(8) Connect the 1st, 2nd, 3rd, 4th and 5th fine tubules,when the pressure displayed by the pressure sensor is basically unchanged, the equilibrium pressure of the 5 fine tubules is recorded at this time;

(9) Other test steps for natural gas with different CO_2 concentrations are repeated (4)~(8).

2.2.2 Experimental Process Without Considering Porous Media

(1) Clean and blow the PVT tube and pipeline, test the temperature and pressure of the instrument, and empty the PVT tube and pipeline ;

(2)Transfer the gas sample (about 100 ml) to the PVT tube;

(3) Constant temperature,constant pressure to the required value of the experiment, stirring stability for 5 hours, and stand for 1 hour, read the volume of gas samples in PVT tube ;

(4) Slowly open the exhaust valve of PVT test unit, and keep the constant pressure of the pump at the formation temperature under the formation pressure to discharge the gas, and use the gas meter to measure the volume of the exhaust gas, and close the exhaust valve. After exhaust, the volume of gas samples in PVT test unit was recorded, and the gas samples discharged were analyzed by chromatography to obtain their composition;

(5) Calculation of deviation coefficient of experimental test by equation (3).

Repeat (5)~ (6)steps at least three times to ensure the accuracy of the deviation coefficient test, that is, the test value is similar, and the relative error should not exceed 2 %.

3 Results and discussion

HP-6890 and Shimadzu GC-14A gas chromatograph are used to analyze the components of each gas sample, and the results are shown in Table 2. Table 2 also provides critical parameters such as critical pressure and critical temperature for each single component. It is worth noting that the CSP7 gas sample is directly obtained from the on-site ground separator, and other gas samples (Gas1, Gas2 and Gas3) are prepared from CSP7 samples, dry gas samples and pure CO_2 gas samples (purity>99.99%) .

The experimental test results of the coefficient of deviation of natural gas with different CO_2 content without considering the porous media are shown in Figure 3. It can be clearly seen from the figure that under the isothermal condition of 80℃ , the coefficient of deviation of natural gas decreases with the increase of CO_2 content. In the low pressure range (approximately <19Mpa), the deviation coefficient of natural gas decreases with the increase of pressure, but in the high pressure range (pressure>19Mpa), the deviation coefficient of natural gas increases with the increase of pressure. The experimental test results considering the coefficient of variation of natural gas with different CO_2 content in porous media are shown in Figure 4. The variation trend of the coefficient of variation with CO_2 content in porous media is consistent with that without considering porous media. When the pressure is less than 17.5MPa, the deviation coefficient of natural gas decreases with the increase of pressure. However, when the pressure is greater than 17.5MPa, the deviation coefficient of natural gas increases with the increase of pressure.

In addition, the comparative results of the experimental tests considering porous media and those without considering porous media are shown in Figure 5. Based on the experimental data, we can clearly see that, under the same pressure, the coefficient of deviation of the porous media is larger than that of the porous media; as the CO_2 content in natural gas increases, the difference between the two gradually increases. Preliminary analysis believes that: the presence of porous media will absorb part of the natural gas, which will reduce the effective gas volume; as the CO_2 content increases, the porous media will absorb more gas because the amount of CO_2 gas adsorbed in the porous media is far greater In the amount of CH_4 adsorbed[21]. As for the change of adsorption capacity, this article will not do a detailed study.

Table2. The composition and the critical parameters of different CO_2 content natural gas

Components	CSP7	Gas1 (mol %)	Gas2 (mol%)	Gas3 (mol%)	P_C/Mpa	T_C/K	ω
CO_2	23.60	0	53.31	87.32	3.394	126.2	0.040
N_2	5.08	0.35	4.43	2.22	7.376	304.2	0.225
C_1	69.99	92.28	41.34	10.25	4.600	190.6	0.008
C_2	1.21	5.69	0.83	0.18	4.884	305.4	0.098
C_3	0.06	1.06	0.05	0.01	4.246	369.8	0.152
iC_4	0.00	0.17	0.01	0	3.640	408.1	0.176
nC_4	0.02	0.21	0.01	0	3.800	425.2	0.193
iC_5	0.00	0.05	0	0.01	3.384	460.4	0.227
nC_5	0.01	0.05	0	0.01	3.374	469.6	0.251
C_6	0.01	0.15	0.01	0.01	2.969	507.4	0.296

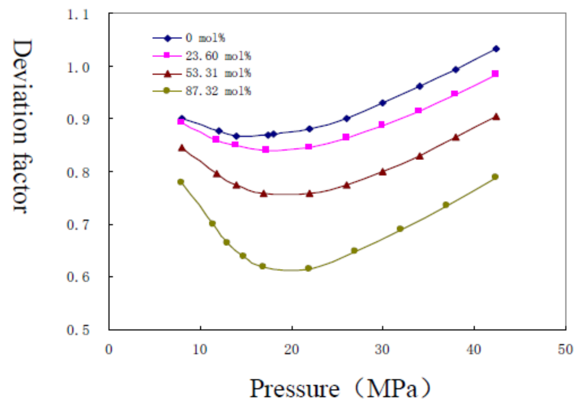


Figure6. Variation of Z-factors of natural gases with different CO_2 content without porous media with pressure at 80 ℃

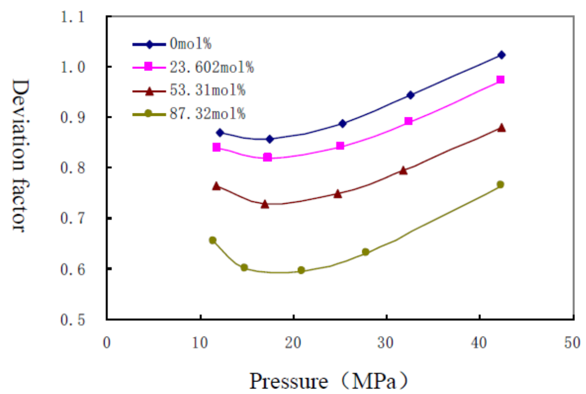
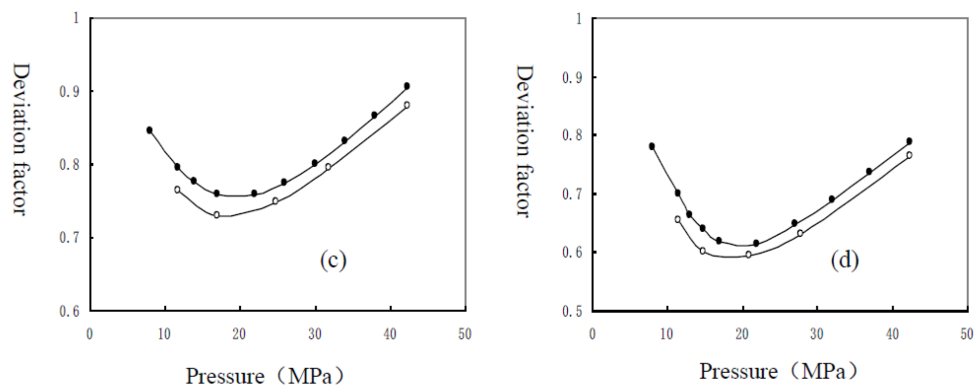
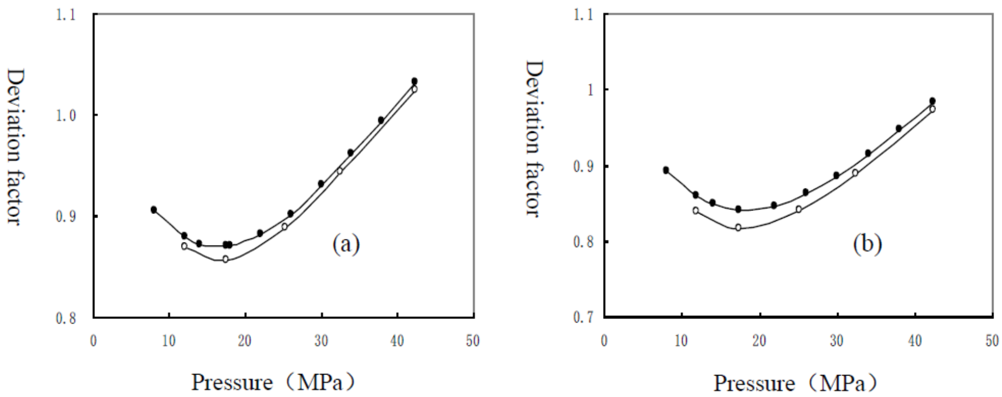


Figure7. Variation of Z-factors of natural gases with different CO_2 content in porous media with pressure at 80 ℃





(a) CO_2=0 mol% (b) CO_2=23.60 mol% (c) CO_2=53.31 mol% (d) CO_2=87.32 mol%

Figure8. The comparison of natural gas deviation coefficient between porous media and non-porous media is considered.

4 Conclusion

In this paper, under the conditions of 80℃ and different pressures (8MPa~42.34MPa), the deviation coefficients of natural gas with different CO_2 content are tested with and without porous media. The experimental results show that, under the condition of constant temperature and pressure, the coefficient of deviation of natural gas with and without porous medium decreases with the increase of CO_2 content in natural gas. Due to the existence of adsorption, under the same temperature and pressure conditions, the deviation coefficient of considering porous media is smaller than that of not considering porous media; with the increase of CO_2 content in natural gas, the difference between the two gradually increases.

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