Experimental study on coalbed methane (CBM) displacement by mixed carbon dioxide and nitrogen

Wenxu She[1,2,3], Junbin Chen[2], Hai Huang[2], Haoping Zhu[3], Jianyong Lei[3], Dazhong Ren[2*], Yunyun Bai[4], Fengjuan Dong[2], Fu Yang[5]

[1]*State Key Laboratory for Continental Dynamics, Department of Geology in Northwest University, Xi'an, Shannxi, China*

[2]*Engineering Research Center of Western Low & Ultra-low Permeability Oilfield Development & Management in Xi'an Shiyou University, Xi'an, Shannxi, China*

[3]*Gas Production Plant 2 of PetroChina Changqing Oilfield Company, Xi'an, Shannxi, China*

[4]*College of Chemistry and Chemical Engineering, Yulin College, Yulin, Shannxi, China*

[5]*Key Laboratory of Coal Resources Exploration and Comprehensive Utilization, Ministry of Land and Resources, Xi'an, Shannxi, China*

Received, July 30, 2018; Accepted November 11, 2018

In order to describe the displacement effect on coalbed methane (CBM) by CO_2 and N_2, the paper takes displacement and replacement efficiency as evaluation parameters. There are 5 gases being taken for indoor displacement experiment on coal samples adsorbed CH_4, i.e. CO_2, N_2 and three mixed gases with different ratio (CO_2:N_2=1:1, CO_2:N_2=1:4 and CO_2:N_2=1:9) under 1.5 MPa, 2.5 MPa, 3.5 MPa, 4.5 MPa and 5.5 Mpa controlled gas injection pressure. Following rules are obtained from the experiments: (1) In terms of displacement efficiency, as the injection pressure increases, displacement efficiency of different gases will increase first and then decrease. (2) In terms of replacement efficiency, replacement efficiency of N_2 shows slow decrease as injection pressure increases, while replacement efficiency of CO_2 shows first increase and then decrease as injection pressure increases. (3) Taking coal samples saturated with CH_4 under 2.5 MPa pressure as an example, the best displacement pressure shall be 2.5-3.5 Mpa. (4) When gas injection pressure is relatively low (lower than 2.0 MPa), the displacement and replacement efficiency of N_2 is higher than that of CO_2, however, under relatively high pressure (higher than 2.0 MPa), the displacement and replacement efficiency of N_2 is lower than that of CO_2. (5) For a mixed gas with a certain mix ratio, for example (CO_2: N_2=1:1), replacement of CO_2 and displacement of N_2 will produce synergistic effect in a certain pressure range (2.5-3.5MPa). Its average displacement efficiency is 86.14%, average replacement is 30.61%, which is higher than the average CO_2 displacement efficiency (83.06%) and average N_2 displacement efficiency (83.39%) but it is lower than the average CO_2 replacement efficiency (34.92%) and higher than the average N_2 replacement efficiency (20.78%).

Key words: Coalbed methane (CBM); Displacement experiment; Carbon dioxide; Nitrogen; Synergistic effect

INTRODUCTION

Coalbed methane (CBM) yields high-quality clean energy. At the same time, under certain conditions, it is also a potential safety hazard for coal mines. The technology of stable and increased production of coalbed methane (CBM) has always been a difficult point restricting the development of coalbed methane (CBM). With successful application of improved coalbed methane (CBM) recovery by CO_2 displacement in the United States [1], this technology has provided new ideas for CO_2 gas storage and coalbed methane (CBM) development. Many scholars have conducted extensive researches on coalbed methane (CBM) production increased technologies by CO_2 and N_2 displacement, with many successful field tests in Poland, Japan, Canada, Netherlands and China **Error! Reference source not found.**. Based on a large number of laboratory experiments and field test data, it is generally believed that the mechanism of coalbed methane (CBM) production increase by gas injection mainly includes two aspects, namely displacement and replacement. Since adsorption capacity of coal to CH_4, CO_2 and N_2 is different, and CO_2 is with the strongest adsorption ability, CH_4 could be displaced by CO_2 due to competitive adsorption effect. At the same time, gas absorption increase in coal will produce expansion effect, resulting decrease of coal permeability and affecting production of coalbed methane (CBM) [8-13]. Therefore, how injected CO_2 and N_2 mixed gas will affect the increased production of coalbed methane (CBM) has become the focus of researches. After the mixed gas is injected, the partial pressure of CH_4 is reduced and desorption begins. In order to avoid CH_4 absorbed back in coalbed after desorption, as well as coalbed permeability decrease caused by a large CO_2 injection, continuous injection of mixed gas is

* To whom all correspondence should be sent:

E-mail: petrogas999@163.com

needed to make the displacement mechanism work. In view of the above process, an indoor laboratory evaluation of the effect of coalbed methane (CBM) displacement by CO_2 and N_2 gas mixture was carried out to determine the optimal gas-displacing coalbed methane (CBM) option.

EXPERIMENTAL COAL SAMPLES, METHOD AND DEVICE

Coal samples preparation

Dafosi coalbed of Jurassic Yan'an formation in western Binxian county, Xianyang city, Shaanxi province was taken as source of experimental coalbed samples. The following are detailed data of the coal samples: average formation pressure is 2.5MPa, average formation temperature is 33°C, gas content of the sampling coalbed is relatively high, between 6.89～16.69 m^3/t, average 11.55 m^3/t. Gas composition in the coalbed is mainly CH_4, gas density is 55.31～89.8%, average 75.76%; N_2 density is 9.79～41.39%, average 22.41%; CO_2 density is 0.32～4.65%, average 1.83%.

Porosity of the coal samples measured by the vacuum pressurized saturated formation water method is generally distributed in the range of 6.05%~10.24%, average porosity is 8.18%. Permeability of the coal samples is between 0.23~0.65 mD, average permeability is 0.45 mD. Porosity and permeability of the coal is relatively low, indicating that the samples belong to compacted coal.

Pulverize the coal samples by a pulverizer, and sieve them with different meshes. Screen 10~120 mesh coal particles and mix them in a certain proportion (Table 1). Put the well-mixed samples into a sand-filling pipe of 100.0 cm length, 4.0 cm diameter, load with 30 MPa overburden pressure until the samples are compacted. Then inject low-pressure non-adsorption helium gas and test. According to the test result, permeability of the sand-filling pipe is 0.55 mD, which is close to the permeability of the original coal sample and meets the experimental requirements.

Table 1. Proportion of coal particles

Mesh	10～20	20～40	40～60	60～80	80～100	100～120	120～160
Proportion	10%	10%	25%	25%	20%	5%	5%

Scheme of experiment

Take 5 gases separately for displacement experiment on coal sample adsorbed CH_4, i.e. CO_2, N_2 and three mixed gases with different mix ratio (CO_2:N_2=1:1, CO_2:N_2=1:4 and CO_2:N_2=1:9) under 1.5 MPa, 2.5 MPa, 3.5 MPa, 4.5 MPa and 5.5 Mpa controlled gas injection pressure. Two indices - displacement efficiency and replacement efficiency - are taken as evaluation parameters. Displacement and replacement efficiency are defined as follows:

Displacement efficiency:

$$\eta = \frac{V_{out}}{V_{add}} \times 100\% \quad (1)$$

where: η: displacement efficiency; V_{add}: CH_4 volume adsorbed in coal samples, mL; V_{out}: volume of CH_4 displaced from coal samples, mL.

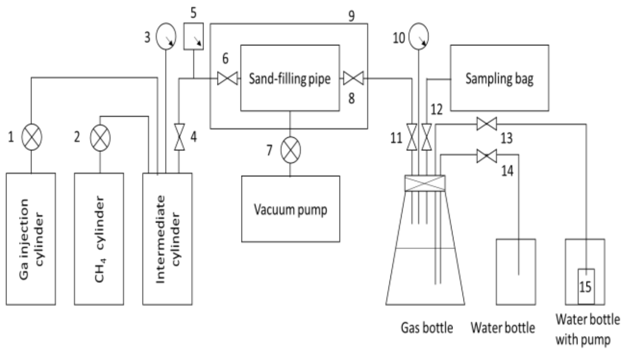
Replacement efficiency:

$$\theta = \frac{V_{out}}{V_{in}} \times 100\% \quad (2)$$

where: θ: replacement efficiency; V_{in}: volume of gas injected into coal samples, mL; V_{out}: volume of CH_4 displaced from coal samples, mL.

Device of experiment

Displacement experiment device consists of a gas injection system, a sand-filling pipe sample chamber system, an intermediate container gas distribution system, a vacuum pumping system, a temperature control system, a drainage gas collection system, and a gas concentration system with gas chromatography analysis.



1，2，4，6，7，11，12，13，14 - Control valves；3，10 - Pressure sensors；5 - Pressure sensor and flowmeter；8 - Backpressure valve；9 - Thermostat box；15 - Submersible pump

Fig. 1. Schematic diagram of the displacement experimental device

Fig. 2. Physical map of the displacement experimental device

Procedure of experiment and calculation method

(1) Procedure of experiment

• Open the three interfaces of the sand-filling pipe, connect vacuum pump, set temperature of thermostat box to 80°C, and evacuate for 24 h;

• Switch thermostat box temperature control system off, open the thermostat box to let sand-filling tube cool off to room temperature for 3 h; Then set temperature of thermostat box to 33°C, close it and stand still at constant temperature for 2 h, turn vacuum pump off;

• Inject CH_4 into intermediate container from the CH_4 cylinder. Open the valve between intermediate container and sand-filling pipe after pressure is constant to make CH_4 enter sand-filling pipe with coal samples. Make it saturated for 12 h. During this operation, the control pressure shall be stabilized around 2.5MPa basically (which is average reservoir pressure);

• Discharge free gas in sand-filling pipe by the drainage gas recovery method. Collect gas by a bottle filled with water and measure volume of water discharged;

• Displace CH_4 gas in coal samples by gas in the gas injection cylinder. Check flow meter No. 5 for volume of injected gas. Collect gas by drainage gas recovery method. Press gas into gas sampling bag by submersible pump and fill water into the gas bottle.

• Measure volumetric concentration of CH_4 gas in sampling bag by a portable gas chromatograph. When displacement starts, measure every 10 min. When concentration of CH_4 is found below 100%, measure every 1 min. In case that three successive numerical changes show less than 5%, it is known that equilibrium state is reached, and the displacement of CH_4 volume could be calculated.

• Change type of gas and way of displacement, repeat the experiment.

(2) Calculation method

According to experimental data, displacement and replacement efficiency could be calculated as follows:

• Intermediate container CH_4 gas balance formula:

$$P_1V_1 = z_1nRT \tag{3}$$

Intermediate container gas balance formula after coal samples in sand-filling pipe are saturated with CH_4:

$$P_2(V_1+V_2) = z_2nRT \tag{4}$$

The following equation can be obtained from formula 3 and formula 4:

$$V_2 = \frac{(z_2P_1 - z_1P_2)V_1}{z_1P_2} \tag{5}$$

where: P_1: initial CH_4 pressure in the intermediate container, MPa; V_1: volume of intermediate container; z_1: initial CH_4 compression factor in the intermediate container; n: amount of CH_4 in the initial intermediate container, mol; R: thermodynamic parameter, 8.31441J/(mol·K); T: absolute temperature, K; P_2: pressure in intermediate container and sand-filling pipe when coal samples are saturated with CH_4, MPa; V_2: pore volume in sand-filling pipe, mL; z_2: CH_4 compression factor when coal samples are saturated with CH_4 in the intermediate container and sand-filling pipe.

• Convert volume of CH_4 in the sand-filling pipe into volume under standard conditions:

$$P_2V_2 = z_2n_1RT \tag{6}$$

$$P_3V_3 = z_3n_1RT \tag{7}$$

$$V_3 = \frac{z_3P_2V_2}{z_2P_3} \tag{8}$$

where: n_1: amount of CH_4 in sand-filling pipe, mol; P_3: gas pressure under standard conditions, 0.1 MPa; V_3: CH_4 gas volume under standard conditions, mL; z_3: CH_4 gas compression factor under standard conditions, 1.

• Residual CH_4 volume in sand-filling pipe after free gas is discharged:

$$V_4 = V_3 - V_5 = V_3 - \frac{m_1}{\rho_1} \tag{9}$$

where: V_4: residual CH_4 volume in sand-filling pipe after free gas is discharged , mL; V_5: volume of free CH_4 gas, mL; m_1: weight of water discharged by free CH_4 gas, g; ρ_1: density of water, g/cm^3.

• Volume of displaced CH_4:

$$V_6 = V_7 \cdot \alpha \tag{10}$$

where: V_6: volume of displaced CH_4, mL; V_7: total gas volume in gas sampling bag, mL; α: volume concentration of CH_4 in the gas sampling bag, %.

- Calculation of displacement efficiency η:

$$\eta = \frac{V_6}{V_4} \times 100\% \tag{11}$$

- Calculation of replacement efficiency θ:

$$\theta = \frac{V_4}{V_8} \times 100\% \tag{12}$$

where: V_8: volume of injected gas under standard conditions, mL.

EXPERIMENTAL RESULTS AND ANALYSIS

Carry out displacement experiments on 5 coal samples saturated with CH_4, by 5 different gases. Set a different injection pressure during the experiments, i.e. 1.5 MPa, 2.5 MPa, 3.5 MPa, 4.5 MPa and 5.5 MPa. Experimental parameters are shown in Table 2 and experimental results are shown in Figure 3.

It can be seen from Figure 3(a) that:

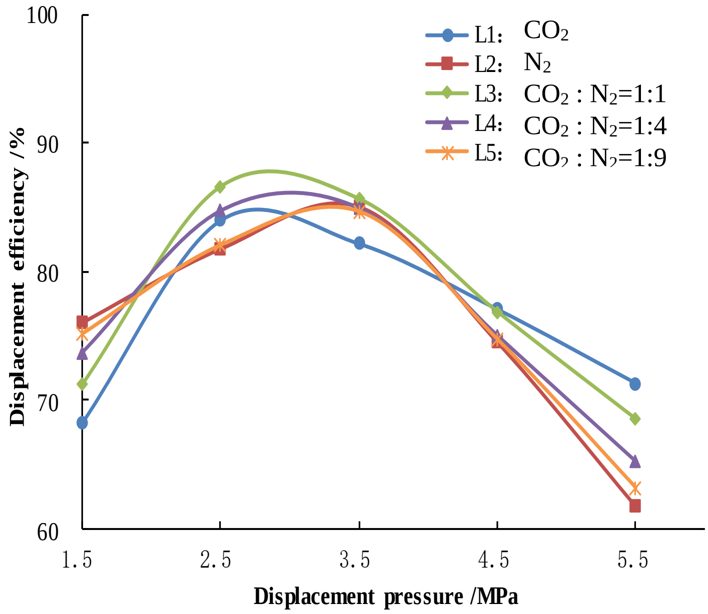
(1) Changing trend of displacement efficiency on CH_4 adsorbed in coal samples by different gases is the same, i.e. displacement efficiency will increase and then decrease along with increasing displacement pressure. The highest displacement efficiency appears when displacement pressure is in the range of 2.5-3.5 MPa.

When displacement pressure increases, it will improve the flow of displacement gas, resulting in an increase of displacement efficiency at the beginning. However, the continuous increase of pressure also makes CH_4 desorption more difficult from the pores of coal samples. The higher the pressure, the less desorption of CH_4 will be, so the displacement efficiency gradually decreases with increasing pressure.

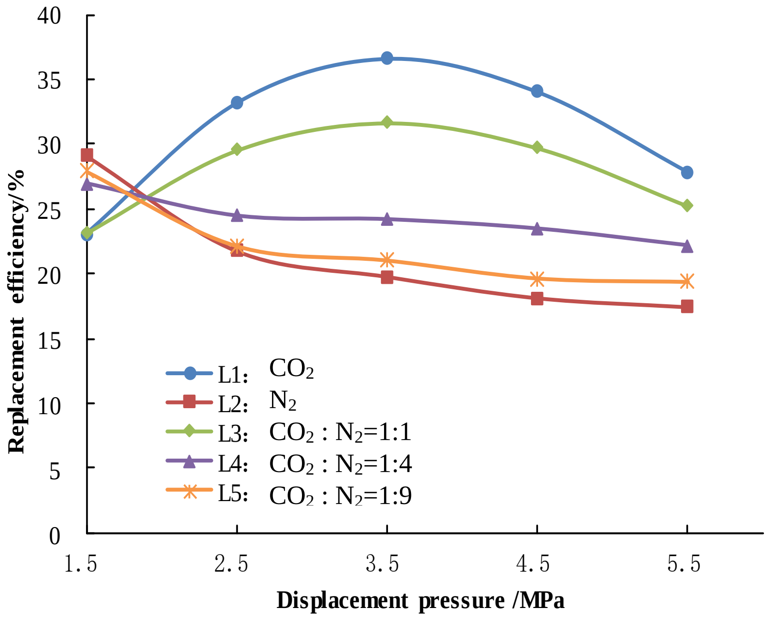
(2) When pressure is relatively low (lower than 2.0 MPa), N_2 has the highest displacement efficiency and CO_2 - the lowest displacement efficiency under the same pressure. When displacement pressure is 1.5 MPa, displacement efficiency of N_2 is 76.01%, and displacement efficiency of CO_2 is only 68.19%. When pressure is gradually increased, displacement efficiency of CO_2 is with the fastest growth, reaching a peak of 83.96% at 2.5 Mpa, while displacement efficiency of N_2 is relatively slow, reaching a peak of 85.03% at 3.5 Mpa.

Table 2. Experimental parameters of gas injection

Gas number	G1 CO_2	G2 N_2	G3 （CO_2：N_2=1：1）	G4 （CO_2：N_2=1：4）	G5 （CO_2：N_2=1：9）
Injection pressure 1.5MPa					
Coal sample number	M1-1.5	M2-1.5	M3-1.5	M4-1.5	M5-1.5
Injection pressure 2.5MPa					
Coal sample number	M1-2.5	M2-2.5	M3-2.5	M4-2.5	M5-2.5
Injection pressure 3.5 MPa					
Coal sample number	M1-3.5	M2-3.5	M3-3.5	M4-3.5	M5-3.5
Injection pressure 4.5MPa					
Coal sample number	M1-4.5	M2-4.5	M3-4.5	M4-4.5	M5-4.5
Injection pressure 5.5MPa					
Coal sample number	M1-5.5	M2-5.5	M3-5.5	M4-5.5	M5-5.5



(a) Curve of displacement efficiency



(b) Curve of replacement efficiency

Fig. 3. Parameter curves of gas injection displacement experiment

As the pressure further increases, displacement efficiency of N_2 rapidly decreases, but the decrease rate of CO_2 displacement efficiency is relatively slow. At 5.5 MPa, the displacement efficiency of CO_2 is reduced to 71.31%, while displacement efficiency of N_2 is only 61.71%.

When pressure is relatively low, CH_4 desorption is mainly controlled by pressure, and competitive adsorption of CO_2 to CH_4 does not affect displacement much. Since displacement pressure is not sufficient to allow gas entering smaller pores, the strong adsorption capacity of CO_2 makes pores in the matrix of coal samples plugged and permeability decreases, the resulting displacement efficiency being smaller than that of N_2. As pressure increases, desorption of CH_4 is suppressed to a certain extent, and the displacement effect caused by competitive adsorption of CO_2 is gradually seen. The higher the CO_2 content, the more obvious the displacement efficiency is driven by replacement effect. Therefore, as pressure increases, CO_2 displacement efficiency is with fastest growth. Under higher pressure, CO_2 displacement efficiency is higher than that of N_2.

(3) In the range from 2.0 to 4.5 MPa, the mixed gas displacement efficiency curve is higher than those of single CO_2 or N_2 indicating that displacement efficiency of the mixed gas is higher than that of single gases in the same pressure range. Among all curves, the curve of L3 and L4 with CO_2: N_2 mixing ratio of 1:1 and 1:4 are the most obvious. Displacement efficiency of L3 reaches 86.61% at 2.5 MPa, which obviously exceeds the displacement efficiency of single CO_2 or N_2 under the same conditions.

Gas injected into the coal sample displaced and replaced CH_4 adsorbed on the pore walls of the coal sample, which is the main mechanism of increasing coalbed methane (CBM) production by gas injection. As the adsorption capacity of CO_2, CH_4 and N_2 gradually decreased in coal samples, replacement of CO_2 is more obvious under the same pressure and temperature, while displacement is the main effect of N_2. Under medium pressure conditions (2.0-4.5 MPa), on the one hand, comparing to the amount of free CH_4 desorption under low-pressure conditions, the amount of free CH_4 desorption is suppressed to a certain extent. In order to displace CH_4, competitive adsorption of CO_2 is required. The higher the CO_2 content, the greater the contribution of displacement will be. On the other hand, in order to avoid desorbed CH_4 absorbed back to coal samples, it is necessary to displace CH_4 by N_2 since N_2 has weaker adsorption capacity than CH_4. The higher the N_2 content, the more contribution of displacement will be. Mixed gas displacement efficiency by synergistic effect from displacement and replacement is better than displacement effect of single gas.

It can be seen from Figure 3(b) that:

(1) There are different characteristics of CH_4 replacement efficiency changing trends in coal samples according to different gases. As pressure increases, CO_2 replacement efficiency increases at first and then decreases. Curve L3 with higher CO_2 content also shows the same trend. Replacement efficiency of N_2 continually decreases as the pressure increases and gradually its trend becomes slow. Replacement efficiency curves L4 and L5 with higher N_2 content also show the same changing trend. Replacement efficiency of mixed gases is generally between displacement efficiency of CO_2 and N_2. According to different proportions of CO_2 and N_2 content, replacement gas efficiency curve of mixed gases is quite different with CO_2 or N_2 displacement efficiency curves.

(2) When pressure is relatively low (lower than 2.0 MPa), replacement efficiency of N_2 is significantly higher than that of CO_2. When displacement pressure is 1.5 MPa, replacement efficiency of N_2 is 29.17% while replacement efficiency of CO_2 is only 23.04%. As pressure increases, replacement efficiency of N_2 smoothly decreases, and replacement efficiency of CO_2 rapidly increases. Replacement efficiency of CO_2 reaches a peak of 36.64% when displacement pressure increased to 3.5 MPa. When displacement pressure reaches 5.5 MPa, displacement efficiency of CO_2 decreases to 27.82% while replacement efficiency of N_2 is 17.43%.

Analysis of curves in Figure 3(b): Mechanism of CO_2 and N_2 injection in coal samples on CH_4 production is different. Under low-pressure conditions, a large number of CH_4 gas molecules start desorption, displacement effect of N_2 plays an important role on coalbed methane (CBM) production, but contribution of CO_2 replacement is not obvious. What's more, due to strong adsorption capacity, matrix micropores plugging of coal samples were decreased, which made CO_2 replacement efficiency less than that of N_2. Although displacement pressure increase could help injecting gas into smaller pores, in order to increase the displacement pressure, it will inevitably increase injection volume. High pressure will also make the CH_4 molecule not easily desorbed; hence replacement efficiency of N_2 will gradually decrease as displacement pressure increases. However, as pressure increases, CO_2 molecules could enter more pores and spread wider. Although pressure increase could cause a decrease of the amount of free CH_4 desorption to some extent, the competitive adsorption of CO_2 could help to displace more CH_4. Thus, CO_2 displacement efficiency gradually increases at the beginning of displacement pressure increase. As pressure further rises, the increase rate of gas injection is greater than the increase rate of CH_4 produced by replacement. Therefore, CO_2 replacement efficiency gradually decreases as the pressure increases.

CONCLUSIONS

Five gases were taken separately for displacement experiment on coal samples with adsorbed CH_4, i.e. CO_2, N_2 and three mixed gases with different mix ratio (CO_2:N_2=1:1, CO_2:N_2=1:4 and CO_2:N_2=1:9) under 1.5 MPa, 2.5 MPa, 3.5 MPa, 4.5 MPa and 5.5 Mpa controlled gas injection pressure. Displacement and replacement efficiency are the key parameters for evaluating the experiment results. The following rules are obtained by comparing the change of displacement and replacement efficiency in each experiment:

(1) Injection pressure of the various gases has different effects on displacement and replacement

efficiency. In terms of displacement efficiency, as the injection pressure increases, displacement efficiency of different gases will first increase and then decrease. In terms of replacement efficiency, replacement efficiency of N_2 shows a slow decrease as injection pressure increases, while replacement efficiency of CO_2 shows first an increase and then decrease as injection pressure increase. Therefore, it is not true that the higher the displacement pressure, the more coalbed methane (CBM) will be developed. Although pressure increase will help gases spread wider to some extent, it also suppresses desorption of CH_4. Taking coal samples saturated with CH_4 under 2.5 MPa pressure as an example, considering the influence of pressure on displacement and replacement efficiency, the best displacement pressure shall be 2.5-3.5 Mpa. In this pressure range, the average displacement efficiency of the 5 injected gases is 84.16%, and the average replacement efficiency is 26.44%.

(2) Under the same injection pressure conditions, different injection gases show different displacement and replacement efficiency. When gas injection pressure is relatively low (lower than 2.0 MPa), replacement of CO_2 is not obvious, displacement and replacement efficiency of N_2 are higher than those of CO_2. As pressure of gas injection increases, the amount of free desorbed CH_4 gradually decreases, and contribution of CO_2 replacement effect to CH_4 development is showing out gradually. Under relatively high pressure (higher than 2.0 MPa), displacement and replacement efficiency of CO_2 is higher than that of N_2. In a certain pressure range (2.5-3.5 MPa), replacement effect of CO_2 and displacement effect of N_2 will generate synergistic effect with a certain proportion of mixed gas (volume ratio of CO_2 and N_2 is 1:1 or 1:4 respectively). Taking mixed gas (CO_2:N_2=1:1) as an example, the average displacement efficiency is 86.14%, average replacement efficiency is 30.61%, which is higher than the average CO_2 displacement efficiency of 83.06% and the average N_2 displacement efficiency of 83.39%. It is lower than the average CO_2 replacement efficiency of 34.92%, but higher than the average N_2 replacement efficiency of 20.78%.

Acknowledgement: *This work was financially supported by the National Natural Science Foundation of China (Grant No.5167040392, 41702146,51874242), China Postdoctoral Science Foundation (2018M643554), Open Fund of State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (Chengdu University of Technology) (PLC20190502) and Project supported by the National Science and Technology Major Project of China: Key Technology of the Tight Gas Enrichment Law and the Exploration and Development(2016ZX05047).*

REFERENCES

1. F. V. Bergen, T. Tambach, H. Pagnier, *Energy Procedia*, **4**, 3112 (2011).
2. F. van Bergen, P. Krzystolik, N. Wageningen, H. Pagnier, B. Jura, J. Skiba, P. Winthaegen, Z. Kobiela, *Int. J. Coal Geol.*, **77**, 175 (2009).
3. M. Fujioka, S. Yamaguchi, M. Nako, *Int. J. Coal Geol.*, **82**, 287 (2010).
4. T. Gentzis, *Int. J. Coal Geol.*, **43**, 287 (2000).
5. C. N. Hamelinck, A. P. C. Faaij, W. C. Turkenburg, F. Bergen, H.J.M Pagnie, O.H.M. Barzandji, K.-H.A.A. Wolf, G.J. Ruijg, *Energy*, **27**, 647 (2002).
6. S. Wong, D. Law, X. Deng, J. Robinson, B. Kadatz, W. D. Gunter, Y. Jianping, F. Sanli, F. Zhiqiang, *Int. J. Greenhouse Gas Control*, **1**, 215 (2007).
7. H. Yu, G. Zhou, W. Fan, J. Ye, *Int. J. Coal Geol*, **71**, 345 (2007).
8. X. Cui, R. M. Bustin, G. Dipple, *Fuel*, **83**, 293 (2004).
9. J. E. Fitzgerald, Z. Pan, M. Sudibandriyo, R.L. Robinson. Jr., K.A.M. Gasem, S. Reeves, *Fuel*, **84**, 2351 (2005).
10. K. Jessen, G. Q. Tang, A. R. Kovscek, *Transport in Porous Media*, **73**, 141 (2008).
11. S. Mazumder, K. Wolf, P. van Hemert, A. Busch, *Transport Porous Media*, **75**, 63 (2008).
12. Y. Tu, C. L. Xie, R. M. Li, S. X. Xie, *Adv. Materials Res.*, **616-618**, 778 (2012).
13. H. Kumar, D. Elsworth, J. Liu, D. Pone, J. P. Mathews, *J. Greenhouse Gas Control*,, **11**, 86 (2012).