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"Gheorghe Asachi" Technical University of Iasi, Romania

METHANOGEN MIGRATION AND ITS EFFECT ON PORE STRUCTURE OF COALS

Hao Chen[1,2,3*], Hongyu Guo[4], Yang Bai[4], Dexun Liu[3], Ze Deng[3]

[1]Key Laboratory of CBM Resource and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, China
[2]School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221008, China
[3]Research Institute of Petroleum Exploration and Development, Beijing 100083, China
[4]School of Energy Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China

Abstract

The migration of methanogen in coal seams have great significance to study the improvement of coal bed gas (CBM) production by injecting microorganisms.This study aims to identify the migration characteristics of methanogens in different rank coals. Methanobacteria migration test was carried out by using coal samples of different particle sizes in the different rank coals. The results show that the maximum relative bacterial absorbance of a Qianqiu mine 18-35 mesh sample was 0.68, higher than that of the corresponding 60-80 mesh sample (0.46), while the corresponding absorbance for the 18-35 mesh and 60-80 mesh samples from Shaqu mine was 0.31 and 0.20, respectively. This suggests that methanogen migration is enhanced by the coals with both larger particle size and lower rank. In order to further study its effect on pore structure, the micron X-CT method was used to analyze the microscopic pore structure. The results show that the methanogen migration improved the coal porosity significantly, with a maximum increase of 8.46% in total porosity and of 10.97% in open pore porosity. This research demonstrates that, given the appropriate environmental conditions, the methanogens can actively migrate in coals and thereby improve coal porosity, which is beneficial to increase CBM production by injecting microorganisms.

Keywords: coal, coalbed methane, methanogens, migration, pore structure

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1. Introduction

Biogenic methane is an important type of CBM resource, because it normally forms after shallow burial and has a low development cost. Consequently, the research on the biogenic CBM has been ongoing for many years. Since their geochemical characteristics show that secondary biogas is present in coalfields and basins around the world (Butland and Moore, 2008; Green et al., 2008; Guo et al., 2012; Tao et al., 2005) a number of researchers have investigated the mechanisms and factors influencing its formation in coal seams (Barnhart et al., 2013; Fang et al., 2015; Flores et al., 2008; Jones et al., 2010; Klein et al., 2008; Liu et al., 2019; Iulianelli et al., 2018; Midgley et al., 2010; Orem et al., 2010; Rotaru et al., 2014; Sapkal, 2018; Satish et al., 2011; Wang et al., 2014).

Several companies (e.g., Apex, Luca Technologies Inc., Next Fuel, and Ciris Energy) have performed field tests at different scales in production wells using a microbially enhanced coalbed methane (MECBM) technique (Ritter et al., 2015), which involves injecting bacteria and nutrients into coal seams, because the methanogens plays a role of "eating" the coal as its metabolic substrate and the nutrients help maintain the stable growth of methanogens. However, the microorganisms in coal seams may migrate along with underground water

*Author to whom all correspondence should be addressed: e-mail: chenhaozg1044@126.com; Phone: +86 18633770498

flows (Zou et al., 2010). This dynamic migration behavior of methanogens is also of great significance to biogas utilization in biological engineering.

In addition, the action of methanogens can affect the porosity of coal. The porosity of coal seam and the migration of methanogens may be a coupling process. Therefore, the change of pore structure after microbial action is also a beneficial exploration. Although the migration of microorganisms in coal could be important, the previous research on the migration of microorganisms in coal is extremely poor. Therefore, in an attempt to understand the migration characteristics of methanogens in different coals, several experiments have been carried out. The change of the pore structures also observed in the coal samples before and after microbiological treatment using methanogens.

2. Material and methods

2.1. Coal samples and methanogens

Coal samples were collected respectively from the mining faces of the Qianqiu coal mine in Henan province and the Shaqu coal mine in Shanxi province (Fig. 1), then proximate analysis was performed by following ISO 17246 Standard. At the same time, the vitrinite reflectance of the samples was measured according to ISO 11760 Standard. The results are shown in Table 1. Mine water samples were collected from the mining faces of the two coal mines mentioned above, sealed at 4°C, and enriched the methanogens using a nutrient solution. The nutrient solution is consisted of 1.0 g NH_4Cl, 0.1 g $MgCl_2 \cdot 6H_2O$, 0.4 g $K_2HPO_4 \cdot 3H_2O$, 0.2 g KH_2PO_4, 0.2 g Na_2S, 2.0 g $NaHCO_3$, 0.001g $C_{12}H_7NO_4$, 0.5 g $C_3H_7NO_2S$, 2.0 g HCOONa, 2.0 g CH_3COONa, 1.0 g yeast and 0.1 g tryptone. The solution was mixed with 10 mL of trace element solution and 1,000 mL of coal mine water, then placed in an anaerobic fermentation device to culture the methanogens at 35°C for four days. Trace element solution: 1000-mL distilled water was mixed with aminotriacetic acid 1.5 g, $MnSO_4 \cdot 2H_2O$ 0.5 g, $MgSO_4 \cdot 7H_2O$ 3.0 g, $FeSO_4 \cdot 7H_2O$ 0.1 g, NaCl 1 g, $CoCl_2 \cdot 6H_2O$ 0.1 g, $CaCl_2 \cdot 2H_2O$ 0.1 g, $CuSO_4 \cdot 5H_2O$ 0.01 g, $ZnSO_4 \cdot 7H_2O$ 0.1 g, H_3BO_3 0.01 g, $AlK(SO_4)_2$ 0.01 g, $NiCl_2 \cdot 6H_2O$ 0.02 g, Na_2MoO_4 0.01 g.

2.2. Experimental setup

The methanogen migration experiment and Micro-X-CT imaging experiment were set up, respectively. The purpose of the methanogen migration experiment was to observe the horizontal migration characteristics of methanogens in the experimental device, which is based on a homemade diffusion device. And Micro-X-CT experiment was to observe the change of pores in coal samples after treatment of bacterial fluid.

2.2.1. Methanogen migration

The homemade diffusion device was shown in Fig. 2. Pairs of glass boxes with dimensions of 200×150×100 mm were constructed and connected together using a 160-mm-long horizontal glass tube with an internal diameter of 30 mm. Then, the horizontal glass tube was filled with coal samples and blocked both ends with strainers to prevent particle leakage. The enriched bacterial liquid of 1000 mL was put into the left glass box, and the same amount of distilled water was put into the right glass box. The 100 g coal samples after sterilization were put into the bacterial liquid and the distilled water, respectively. Four identical devices were constructed and filled with Qianqiu 18-35 mesh, Qianqiu 60-80 mesh, Shaqu 18-35 mesh, and Shaqu 60-80 mesh coal samples in the horizontal glass tube, respectively. The diffusion device was filled with nitrogen to ensure the anaerobic environment and put into a constant temperature incubator at 35°C. Then the migration characteristics of methanogens through the horizontal glass tube from bacterial liquid to the distilled water were analyzed by detecting the change of liquid absorbance.

Fig. 1. The location of coal samples

Table 1. Proximate analyses of coal samples

Source	M_{ad}/%	V_{daf}/%	A_d/%	$R_{o,ran}$/%
Qianqiu mine	0.98	10.31	40.01	0.56
Shaqu mine	0.42	7.35	23.53	1.51

Abbreviations: M, moisture; ad, air dry basis; V, volatile matter; daf, dry and ash-free basis; A, ash yield; d, dry basis; $R_{o,ran}$, random vitrinite reflectance

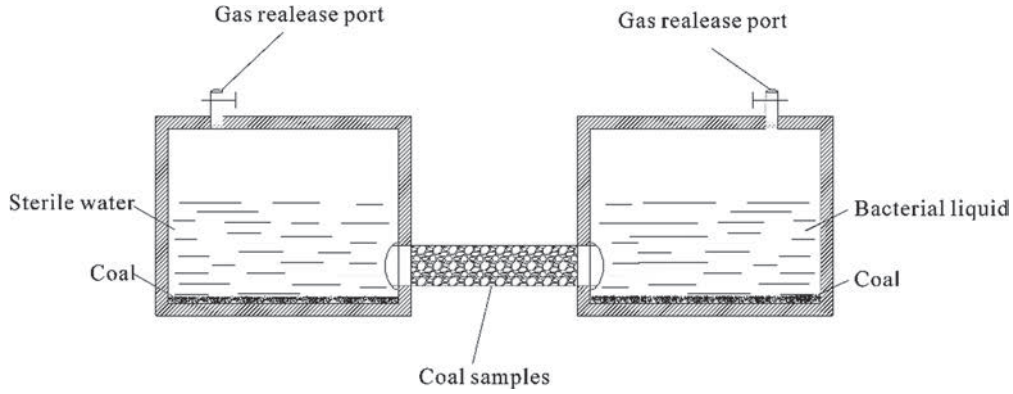

Fig. 2. Experiment device of Methanogen migration

2.2.2. Micro-X-CT imaging

Coal samples were polished into pillarswith a diameter of 6mm and a height of 10 mm, denoted as Y-1 and Y-2 (Qianqiu), and S-1 and S-2 (Shaqu). Then, Micro-CT imaging was used to observe the pore structures from pillar samples. The Micro-X-CT imaging process was repeated twice, firstly, after treating the samples with deionized sterile water for 15 days and after treating them with bacterial liquid for 15 days.

2.3. Analytical instruments

The bacterial absorbance was measured with a spectrophotometer (UV-5200; Shanghai Metash, Shanghai, China) at wavelengths of 190-1,100 nm with ±0.8 nm wavelength accuracy, ±0.2 nm wavelength reproducibility, ±0.3% T photometric accuracy, and at most 0.1% T stray light.

In addition, the pore structure of the coal samples were imaged using a μ225kV Micro-CT system (Institute of Applied Electronics, China Academy of Engineering Physics, Mianyang, China), equipped with X-ray and digital flat panel detectors. The X-ray machine had a minimum focus size of 3 μm, a ray cone angle of 25°, a minimum focal length of up to 4.5 mm, and a high-voltage range of 10-225 kV. The flat panel detector had a 406 × 293 mm^2 imaging window (i.e., 3,200 × 2,304 probes), and a frame rate of 1-30 frames/s.

3. Results and discussion

3.1. Methanogen migration

The results show that, in each case, the absorbance of the sterile water in the left glass box gradually increased until day eight, indicating the methanogens were migrating from right to left (Table 2). After day eight, the absorbance decreased gradually, likely due to the fact that the sterile water environment was not conducive for the methanogens to survive. The fluctuations seen in the absorbance of the bacterial liquid in the right glass box over the 15 days of this experiment may be due to the methanogens growing and migrating to the left (Fig. 3). Because the the diffusion device was in a closed environment, the change of liquid absorbance was mainly caused by the growth and metabolism of bacteria and the balance of left and right liquid. From the observation of absorbance, it was not a typical bacterial growth curve, so it was speculated that there are diffusionaction.

Relative absorbance values also calculated based on the ratio of the absorbance of the sterile water on the left side to that of the bacterial liquid on the right side (Fig. 4). The higher the relative absorbance, the higher the migration efficiency. Comparing coal samples with different particle sizes, the maximum relative absorbance of the Qianqiu 18-35 mesh sample was higher than that of its 60-80 mesh counterpart. Likewise, the maximum relative absorbance of the Shaqu 18-35 mesh sample was higher than that of the 60-80 mesh sample. Sharma et al. have proved that the migration of microorganisms in porous media is closely related to the pore size of soil (Sharma et al., 1993).

Barton and Ford, (1995) found that with the increase of sample size in the soil column, the speed of microbial migration increased The results in this work also suggest that larger coal particle sizes significantly increase methanogen migration efficiency. Similarly, comparing samples from different mines with similar particle sizes but different coal ranks reveals that the maximum relative absorbances of the Qianqiu 18-35 mesh and 60-80 mesh samples were both higher than those of their Shaqu counterparts. These results suggest that methanogen migration is much more efficient in low-rank coals.

Table 2. Absorbance after 15 days of migration

Time (days)	*Qianqiu, 18-35 mesh*			*Qianqiu, 60-80 mesh*			*Shaqu, 18-35 mesh*			*Shaqu, 60-80 mesh*		
	Bacterial liquid	*Sterile water*	*Relative absorbance*	*Bacterial liquid*	*Sterile water*	*Relative absorbance*	*Bacterial liquid*	*Sterile water*	*Relative absorbance*	*Bacterial liquid*	*Sterile water*	*Relative absorbance*
1	0.239	0.011	0.05	0.226	0.021	0.09	0.324	0.021	0.06	0.395	0.030	0.08
2	0.215	0.029	0.13	0.345	0.022	0.06	0.535	0.040	0.07	0.434	0.021	0.05
3	0.342	0.142	0.42	0.328	0.042	0.13	0.547	0.082	0.15	0.418	0.024	0.06
4	0.366	0.210	0.57	0.316	0.048	0.15	0.489	0.103	0.21	0.496	0.022	0.04
5	0.337	0.230	0.68	0.325	0.104	0.32	0.502	0.134	0.27	0.530	0.048	0.09
6	0.325	0.210	0.65	0.375	0.118	0.31	0.544	0.144	0.26	0.486	0.082	0.17
7	0.371	0.219	0.59	0.318	0.124	0.39	0.560	0.162	0.29	0.427	0.079	0.19
8	0.335	0.190	0.57	0.309	0.132	0.43	0.499	0.154	0.31	0.391	0.052	0.13
9	0.349	0.176	0.50	0.316	0.126	0.40	0.572	0.153	0.27	0.387	0.061	0.16
10	0.305	0.128	0.42	0.267	0.106	0.40	0.633	0.123	0.19	0.388	0.051	0.13
11	0.387	0.103	0.27	0.288	0.119	0.41	0.572	0.102	0.18	0.345	0.068	0.20
12	0.402	0.067	0.17	0.213	0.092	0.43	0.403	0.060	0.15	0.359	0.057	0.16
13	0.289	0.059	0.20	0.269	0.072	0.27	0.457	0.045	0.10	0.367	0.075	0.20
14	0.392	0.071	0.18	0.201	0.092	0.46	0.393	0.074	0.19	0.433	0.070	0.16
15	0.303	0.068	0.22	0.214	0.064	0.30	0.349	0.060	0.17	0.409	0.049	0.12

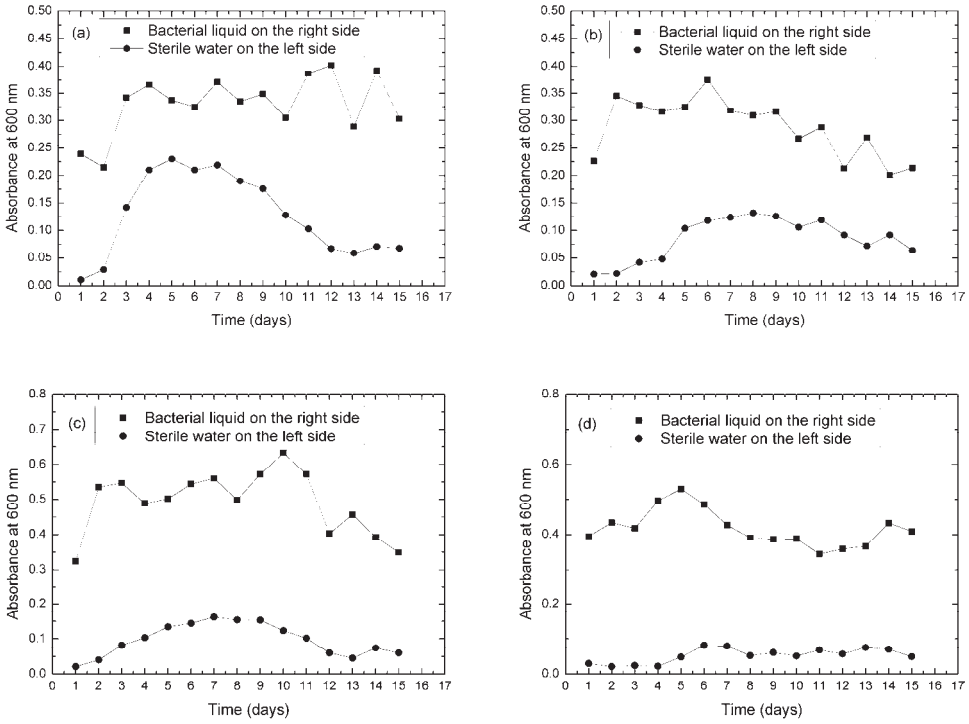

Fig. 3. Migration characteristics of methanogen (a) Qianqiu 18-35 mesh, (b) Qianqiu 60-80 mesh, (c) Shaqu 18-35 mesh, and (d) Shaqu 60-80 mesh samples

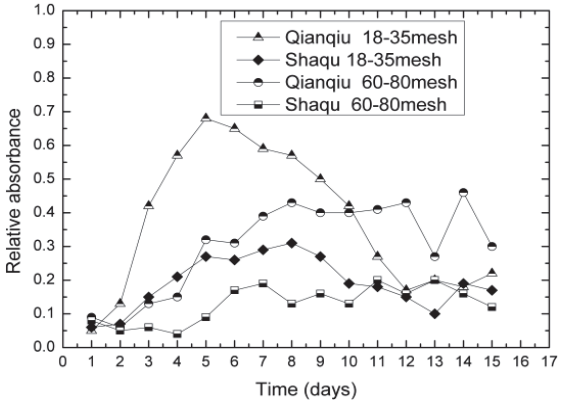

Fig. 4. Relative absorbance of the different coal samples

There are two possible reasons: Firstly, the low rank coal is more easily degraded and utilized by methanogenes, so it is conducive for methanogen to pass through the horizontal glass tube filled with low-rank coal samples (Fallgren et al., 2013; Robbins et al., 2016). Secondly, Qianqiu coal samples have higher porosity, and the higher porosity, the more conducive to the migration of methanogens. Therefore, particle size and coal rank are two of the key factors influencing migration efficiency. Coal pillars filled with large particles are more permeable, increasing their migration efficiency. Similarly, methanogens are more active and thus migrate more easily in low-rank coal.

3.2. Effect of migration on pore structure

A total of 1,500 image slices by Micro-CT scanning generated, then evaluated them using Avizo 9.0 software (FEI Company, Hillsboro, Oregon, USA). These were scanned at intervals of 3.89 μm in the longitudinal direction, and we used slices 650-850 to reconstruct a three-dimensional visualization model, namely a cube with dimensions of 200×200×200 pixels (i.e., 0.778×0.778×0.778 mm). The three-dimensional pore distribution of the coal sample was reconstructed using the two-dimensional slice gray-scale image as the material and avizo 9.0.1 software (Fig. 5). The pore structure analysis results are shown in Table 3.

These results show that the total porosities of all the coal pillars increased when they were treated with bacterial liquid rather than water (Fig. 5). In particular, the porosities of samples Y-1 and Y-2 increased by 8.46% and 6.56%, respectively, which are significantly greater than the increases seen in samples S-1 (1.06%) and S-2 (1.77%). The results also show that the porosity of the open pores in samples Y-1 and Y-2 increased by 10.97% and 6.14%, respectively, changes that are again greater than those seen in samples S-1 (0.42%) and S-2 (1.39%). Taken together, these results show that there were significantly greater porosity increases in the coal from the Qianqiu mine than in that from the Shaqu mine (Table 3). When comparing coal samples of similar rank, the ratio of the increase in total pore porosity to that in the open pore porosity was higher for sample Y-1 than for sample Y-2, but lower for sample S-1 than for sample S-2. Because of the open pore porosities of samples Y-1 and S-2 after treatment with water were much higher than those of samples Y-2 and S-1, respectively, the methanogens were able to migrate more easily in samples Y-1 and S-2, significantly expanding the pores.

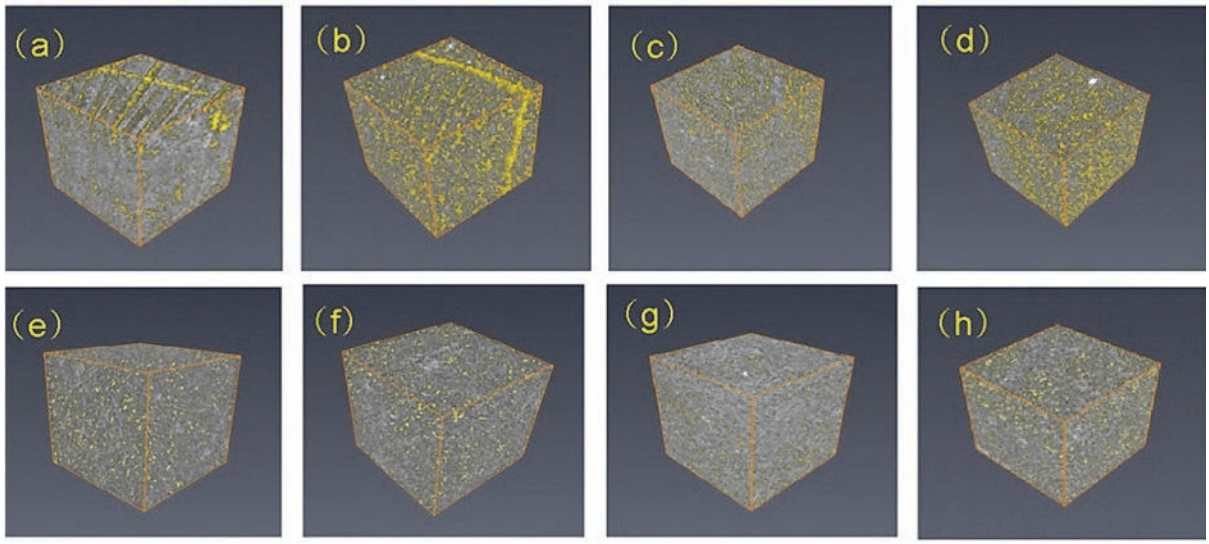

Fig. 5. Three-dimensional reconstructions from Micro-CT images of different coal samples: (a) Y-1 treated with water, (b) Y-1 treated with bacterial liquid, (c) Y-2 treated with water, (d) Y-2 treated with bacterial liquid, (e) S-1 treated with water, (f) S-1 treated with bacterial liquid, (g) S-2 treated with water, (h) S-2 treated with bacterial liquid

Table 3. Changes in coal sample porosity with treatment

Sample	*Pretreatment method*	*Total porosity (%)*	*Increase in total porosity (%)*	*Open pore porosity (%)*	*Increase in open pore porosity (%)*
Y-1	Water	5.72	8.46	3.06	10.97
	Bacterial liquid	14.18		14.03	
Y-2	Water	5.93	6.56	2.05	6.14
	Bacterial liquid	12.49		8.19	
S-1	Water	3.12	1.06	0.83	0.42
	Bacterial liquid	4.18		1.25	
S-2	Water	4.15	1.77	1.08	1.39
	Bacterial liquid	5.92		2.47	

4. Conclusions

The results of this study reveal the migration behavior of methanogens in coal samples: migration is faster for larger coal particle sizes and lower-rank coal. In addition, Micro-CT images show that methanogen migration can increase the porosity, improve the connectivity of pore structures, and increase the permeability. Methanogen migration in coal seams thus increases coal reservoir permeability and vice versa, it is an aspect worthy of consideration for CBM bioengineering in the future.

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