Effect of Cyclical Microwave Modification on the Apparent Permeability of Anthracite: A Case Study of Methane Extraction in Sihe Mine, China

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ABSTRACT: The application of cyclical microwave modification for accelerating the extraction of coalbed methane (CBM) from anthracite is limited. In this study, the apparent permeability of anthracite samples before and after each microwave treatment (three in total) for 120 s was measured by a self-built permeability-testing platform. Microcomputed tomography (micro-CT) technology and image-processing technology were employed to analyze the 3D micron-scale pore structures, especially the quantitative characterization of connected pores and throats. After modification, the average apparent permeability increased from 0.6 to $5.8 \times 10^{-3}$ μm$^2$. The generation, expansion, and connection of micron-scale pores and fractures became more obvious with each treatment. The total porosity increased from 3.5 to 6.2%, the connected porosity increased from 0.9 to 4.8%, and the porosity of isolated pores decreased from 2.5 to 1.4% after three cycles. The number, volume, and surface area of the connected pores as well as the number, radius, and surface area of the throats were significantly increased. In addition, the release of alkyl side chains from the anthracite surface reduced the capacity of the anthracite to adsorb CH$_4$ and the decomposition of minerals promoted the development and connectivity of pores. As a result, the gas seepage channels have been greatly improved. This work provides a basis for micron-scale pore characterization after cyclical microwave modification and contributes to CBM extraction.

1. INTRODUCTION

Coalbed methane (CBM) provides a clean energy supply for the world. Since the 1970s, CBM has developed into a sustainable commodity with a great economic value in the United States and Canada. The CBM reserves in China are approximately $36.81 \times 10^{12} \text{m}^3$ and rank third after Russia and Canada. In the past, CBM was only discharged to avoid coal/gas outbursts or gas explosions during coal production. It was not until 2003 that the first commercial well for CBM extraction in China was reported. Subsequently, China’s CBM extraction industry developed rapidly. However, the efficiency of CBM extraction is extremely low in most areas due to poor geological conditions such as low permeability and low porosity, which restricts the commercialization process.

Many approaches have been considered in the effort to stimulate coal reservoirs. Methods other than CO$_2$ substitution and N$_2$ displacement will have a significant effect on reservoir permeability. One approach is fluid injection, which includes hydraulic, high energy gas, supercritical CO$_2$, liquid nitrogen, and steam injection fracturing. Another approach is the application of external acoustic, electric, electromagnetic, or electrochemical fields. Although these methods have achieved enhancements, there are still some limitations, such as water locking damage, construction costs, complex operations, ecological environmental pollution, and even the possibility of inducing earthquakes by hydraulic fracturing. At present, microwave modification technology has been successfully used for coking, reduction of energy for pulverization, lignite dehydration, coal desulfurization, low-rank coal pyrolysis, biomass pyrolysis, enhancing flotation, auxiliary rock breaking, heavy oil exploitation, and oil shale exploitation.

Microwave modification can increase the temperature of the coal or rock stratum and aid in moisture removal. Microwave radiation heating is a highly efficient and environmentally benign method for reservoir stimulation due to its unique instantaneous
effects, overall penetrability, selectivity, and controllability. Microwaves are electromagnetic waves with frequency in the 300 MHz to 300 GHz range. The essence of the heating effect is dielectric relaxation; that is, under the effect of an electric field, the dipole moments of polar molecules rotate. When the electric field frequency is equal to the microwave frequency, the rotation speed of electric dipoles cannot keep up with the frequency of the microwave electric field, resulting in a hysteresis phenomenon. Hong et al., Xu et al., and Huang et al. carried out simulations of the heating behavior of coal under microwave radiation using COMSOL and reported that microwaves can rapidly heat coal. Cai et al., Teng et al., and Zhao et al. found that the pore structures and permeability of coal change under high-temperature conditions. Wang et al. found that high temperatures can induce cracks in the hot dry rock and improve its brittleness index and even increase its permeability by an order of magnitude.

Micro-CT is a high-efficiency method to analyze micron-scale pores, fractures, cracks, and cleats without causing any structural damage in coal samples. Feng and Zhao observed the characteristics of mesocrack evolution in lignite and gas coal with temperature variation. Kang et al. observed and analyzed the thermal cracking process of oil shale from 20 to 600 °C. The structural parameters of micron-size pores can be characterized quantitatively by the postprocessing of images. Kong et al. measured the pore-fracture features of anthracite such as pore number, porosity, and average pore diameter before and after electrochemical modification combined with MATLAB software. Huang et al. studied the connectivity of the pores and fractures in oil shale at different steam temperatures by digitization of cores. Kumar et al. determined the cleat frequency and distribution in two cores and confirmed that new fractures were induced by exposure to high-energy microwaves. Yao et al. demonstrated the capability of micro-CT to characterize the development of coal porosity and fractures and found that the distribution characteristics of porosity were highly anisotropic. Cai et al. examined the evolution of a 3D fracture network under stress until failure occurred by micro-CT and acoustic emission.

In this paper, the apparent permeability was studied for anthracite samples before and after they underwent cyclical microwave modification; measurements were performed with a permeability-testing platform that was built in this laboratory. The structure of micron-scale pores before and after modification, especially the connected pores that make the main contribution to gas seepage in anthracite, were quantitatively characterized by micro-CT combined with the image-processing technology. Moreover, the surface groups on
anthracite and the minerals in the coal were investigated by Fourier transform infrared (FTIR) spectroscopy.

2. RESULTS AND DISCUSSION

2.1. Influence of Cyclical Microwave Modification on the Apparent Permeability of Anthracite. Apparent permeability plays an important role in the evaluation of recovery efficiency of CBM extraction. Li et al. found that the apparent permeability of anthracite in Qinshui Basin is in the range of $0.01 \times 10^{-3}$ to $10 \times 10^{-3} \mu m^2$. The variation law of apparent permeability of anthracite after cyclical microwave modification is shown in Figure 1a, and the variation fitting results are shown in Figure 1b. It can be seen that the apparent permeability of the raw anthracite sample was in the range of $0.5−0.7 \times 10^{-3} \mu m^2$, and the results were consistent with Li et al. After microwave exposures for 1, 2, and 3 cycles, the average apparent permeability increased from 0.6 to 3.6, 5.0, and $5.8 \times 10^{-3} \mu m^2$, increasing by 5.1, 7.4, and 8.8 times, respectively. The results showed that improving apparent permeability by cyclical microwave modification can effectively accelerate the extraction of CBM. The modification mechanism would be analyzed by the changes in microscale pore structures, surface groups, and mineral materials in anthracite.

2.2. Influence of Cyclical Microwave Modification on the Porosity of Anthracite. The change in pore structures after three cycles of microwave exposure is exhibited in a 3D representative volume element (3D-REV) in Figure 2. The porosity of the total pores and connected pores increased, while the porosity of the isolated pores decreased with cyclical microwave modification, as shown in Figure 3. The total porosity increased from 3.5 to 6.2% and the connected porosity increased from 0.9 to 4.8%, increases of 77.6 and 409.6%, respectively. The porosity of isolated pores decreased from 2.5 to 1.4%, a reduction of 45.3%.

This phenomenon indicated that microwave radiation had an obvious effect on the generation, expansion, and connection of micron-sized pores and fractures, which could be attributed to several factors. Images were obtained using micro-CT scanning at the same positions before and after three cycles of microwave modification, as shown in Figure 4. New micron-scale pores developed in zone A1, and the micron-scale pores and fractures in zone A2 became wider. The main reason for these changes was that the moisture in pores quickly evaporates and expands when stimulated by microwave radiation; this behavior may open some closed pores. The residual water in the coal matrix and part of the water bound to the minerals evaporate and is removed under microwave radiation; the high-pressure steam creates new pores, widens the original pores, and increases the pore connectivity. It can be seen that in zone A3, new cracks formed at the coal–mineral interfaces because the thermal conductivities and thermal expansion coefficients differ for coal and minerals, causing different temperature increases in coal and minerals under microwave irradiation. In addition, the high temperature (locally up to 369 °C after 120 s of microwave irradiation) causes thermolysis in the macromolecular structure of coal. We can see in zone B that some minerals that were removed under microwave irradiation led to the formation of new micron-scale pores. The reason for the formation of new pores may have been that the microwaves catalyzed the chemical reaction of pyrite (FeS$_2$) in the coal with the surrounding H$_2$O, O$_2$, or small molecules such as H$_2$O, CO, and CO$_2$ adsorbed in the coal; these reactions may have released gases such as H$_2$S, SO$_2$, and carbonyl sulfide (COS). Besides, some minerals may have been displaced and fallen into the fractures in more highly fractured regions.

2.3. Quantitative Characterization of Connected Pores and Throats before and after Cyclical Microwave Modification. The pores and throats of connected pores in the 3D-REV were characterized quantitatively based on a pore network model (PNM). Figure 5 shows the changes in pore parameters in the 3D-REV before and after cyclical microwave modification. The pore number, pore volume, and pore surface area all increased at first and then decreased with increasing pore radius. The total number of connected pores increased from 2651 to 10,020, the total volume increased from 8.9 to 45.3 mm$^3$, and the total area increased from 609.2 to 1899.6 mm$^2$, the increase being 278, 410, and 212%, respectively. The number of pores with a radius of 70 $\mu m$ corresponded to the maximum in the pore size distribution before and after modification, 417 and 1394, respectively. The maximum values of the pore volume and surface area occurred for pores with the maximum radii of 130 and 90−130 $\mu m$, respectively, after modification and 90−100 $\mu m$ (both) before modification. The increase due to modification was the largest for the total volume of connected pores, which indicated that some of the pores became larger under the action of microwave radiation. The increase was larger for the total number of connected pores than the surface area, indicating that some isolated pores developed into connected pores during the modification process.

The throat parameters can essentially reflect the connectivity of pores. Figure 6 shows the throat parameters of the 3D-REV before and after cyclical microwave modification. The number of throats increased from 6607 before modification to 33,120 after modification; similarly, the maximum throat radius increased from 110 to 260 $\mu m$, and the maximum throat length decreased from 2710 to 1430 $\mu m$. The largest contributions to the throat surface area were throats with radii of 0−100 $\mu m$ before modification and radii of 0−200 $\mu m$ after modification. The decrease in throat length and increase in throat radius and surface area all indicated that the pore connectivity was better after modification.

The pore coordination number represents the mutual configuration relationship between pores and throats, which is numerically equal to the number of throats connected to a pore. Figure 7 shows the relationship between the pore number and the pore coordination number before and after modification. The number of pores with coordination numbers less than 10 was 2591 (98% of the total) before modification and 9427 (94%) after modification. The maximum pore coordination...
number increased from 22 before modification to 29 after modification. The number of connected pores increased and that their connectivity improved due to cyclical microwave modification.

2.4. Change in Surface Groups on Anthracite and Minerals in Anthracite. The surface groups and minerals can affect the gas seepage behavior by influencing the adsorption/desorption of methane and pore structures in anthracite. The chemical bonds in sulfur-containing groups such as mercaptans (−SH), thioethers (−S−), and thiophenes (−C4H4S) in the coal macromolecular structure break when they resonate with the electromagnetic microwaves, and some alkyl side chains and oxygen-containing functional groups in coal are pyrolyzed and released as gas. The peaks near 2925 and 2855 cm\(^{-1}\) are identified as the stretching vibrations of −CH\(_2\) and −CH\(_3\), respectively. The peaks near 2515 and 460 cm\(^{-1}\) are attributed to the vibrations of S−H. The peak at 1600 cm\(^{-1}\) corresponds to the vibrations of C═O and C═C. The peak at 1430 cm\(^{-1}\) is identified as the bending vibration of −CH\(_3\) and the antisymmetric stretching vibration of carbonate groups. The peak near 1030 cm\(^{-1}\) is attributed to the stretching vibrations of Si−O−Si and Si−O−C. The adsorption peaks near 2925, 2855, and 1430 cm\(^{-1}\) are slightly smaller for modified samples than unmodified samples, indicating that some of the methyl and methylene groups were removed and the adsorption capacity of coal was weaker. Figure 8 shows the FTIR results for surface groups on anthracite samples before and after cyclical microwave modification. The peaks near 2925 and 2855 cm\(^{-1}\) are identified as the stretching vibrations of −CH\(_2\) and −CH\(_3\), respectively. The peaks near 2515 and 460 cm\(^{-1}\) are attributed to the vibrations of S−H. The peak at 1600 cm\(^{-1}\) corresponds to the vibrations of C═O and C═C. The peak at 1430 cm\(^{-1}\) is identified as the bending vibration of −CH\(_3\) and the antisymmetric stretching vibration of carbonate groups. The peak near 1030 cm\(^{-1}\) is attributed to the stretching vibrations of Si−O−Si and Si−O−C. The adsorption peaks near 2925, 2855, and 1430 cm\(^{-1}\) are slightly smaller for modified samples than unmodified samples, indicating that some of the methyl and methylene groups were removed and the adsorption capacity of coal was weaker. The decrease in CH\(_4\) adsorption indicated that the gas seepage performance in coal was improved.
because of the coal matrix shrinkage effect.\textsuperscript{72,73} The intensities of absorption peaks near 2515, 1030, 540, and 460 cm\textsuperscript{-1} decreased notably after modification of the samples, indicating that microwave radiation broke some sulfur-containing bonds and decomposed some minerals, such as sulfur, carbonate, and silicate. The decomposition of minerals would increase the pores in anthracite. This phenomenon is also observed in the micron-scale pores and fractures shown in Figure 4 (zone B).

3. APPLICATION AND SIGNIFICANCE

Microwaves can heat the reservoir rapidly within the distance that microwaves penetrate. The penetrability and controllability of microwaves make their heating efficiency higher and more convenient than traditional conduction heating. More importantly, the whole modification process causes limited pollution of the environment. Therefore, in the field of engineering applications, the cyclical microwave modification method can not only inhibit methane adsorption and accelerate methane seepage but also make a significant contribution to environmental protection.

Figure 9 shows a schematic diagram of the method for accelerating CBM extraction by microwave radiation combined with water injection. Microwave treatment and water injection are performed alternately by the system. High-pressure steam produced by rapid vaporization of water by microwaves can cause cracks to grow rapidly and relieve water locking damage caused by water injection. The cyclical temperature impact makes the coal reservoir expand and contract repeatedly, which is conducive to the development of pores and fractures. Yang and Liu\textsuperscript{15} used experiments and modeling to study the changes in the pore structure of coal that were induced by cyclic nitrogen injections, they found that the total volume of mesopores (2–50 nm) and macropores (>50 nm) increased with cryogenic...
treatment, while the growth rate of pore volume decreased with increasing numbers of freeze—thaw times.

4. CONCLUSIONS

(1) For accelerating CBM extraction, the influence of cyclical microwave modification on the apparent permeability of anthracite in Sihe mine, China, was studied, and the change in microscale pore structures, surface groups, and minerals in anthracite before and after microwave modification was measured.

(2) With the increase in cyclical microwave modification times, the apparent permeability of anthracite increased continuously due to the continuous increase in the quantity and connectivity of micron-scale pores.

(3) The gasified release of alkyl side chains on anthracite surface reduced the CH₄ adsorption capacity, and the decomposition of mineral materials in anthracite increased the micron-scale pores.

(4) The changing law of anthracite apparent permeability after three times of single power microwave modification has been researched. The effect of cyclical microwave modification on various metamorphic degree coals with different electric powers and different cycles will be further studied to achieve more parameters for in situ engineering application.

5. EXPERIMENTAL SECTION

5.1. Sample Preparation. The anthracite coal samples for the cyclical microwave treatment experiment were obtained...
from the 15,303 freshly exposed working face of the Sihe mine of the Qinshui coalfield, Shanxi Province, China. The large lumps of coal were carefully selected and immediately packed in plastic wrap and sealed in bags, and then, they were sent to the laboratory as soon as possible to avoid changes in their physicochemical properties due to oxidation. The coring direction was perpendicular to the bedding of the large lumps of coal, and the cylindrical samples were polished to a size of 50 mm diameter and 50 mm height. In addition, powdered samples with a size of 60–80 mesh were prepared. The mean maximum vitrinite reflectance ($R_{\text{max}}$), the proximate analysis, the elemental composition, and the maceral composition of the anthracite were determined following the standards GB/T 6948-2008, GB/T 212-2008, GB/T 476-2001, and GB/T 8899-2013, respectively. The analysis results are listed in Table 1.

5.2. Experimental Apparatus. The tests of apparent permeability of the anthracite samples before and after cyclical microwave modification were conducted using a self-built permeability-testing platform. Figure 10 shows the schematic of the experimental apparatus. The device is mainly composed of a vacuum-pumping system, a confining pressure-loading system, an inlet/outlet system, and a measuring system. Before the test, the coal samples and the porous metal gaskets at both ends were placed together in the sealing sleeve and were sealed between the base and the axial piston with two sealing rings.

The cyclical microwave modification experiment of the anthracite samples was carried out in a P70F20CL-DG(B0) microwave oven produced by Guangdong Galanz company. The dimensions of the resonator in the oven were 180 mm high, 315 mm wide, and 329 mm deep. The frequency of the microwave oven was $2.45 \times 10^9 \pm 50$ Hz. The maximum power was 700 W and could be adjusted.

The micro-CT scanning of the anthracite samples was conducted with a nanoVoxel-4000 open tube reflective high penetration CT system produced by Sanying Precision Instruments Co., Ltd. The scanning voltage was 150 kV, the scanning current was 150 $\mu$A, the exposure time was 3.5 s, and the spatial resolution was 19.6 $\mu$m. Sixteen-bit images with $3000 \times 3000 \times 3000$ voxels were obtained after the whole sample was scanned and processed.

The analysis of the surface groups of the anthracite samples was performed using a Nicolet i55 FTIR instrument produced by Nicolet, USA. The spectra were collected in the range of 4000 to 650 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ and 32 scans for each sample. The analysis results are listed in Table 1.
anthracite can be calculated using eq 1.74 and a response time of 500 ms.

\[ k_a = \frac{2qP_{\text{fl}} \mu L}{A(R_i^2 - R_o^2)} \]  

where \( k_a \) is the apparent permeability of the anthracite sample \((10^{-3} \, \mu \text{m}^2)\), \( q \) is the flow rate of the CH\(_4\) \((\text{cm}^3/\text{s})\), \( \mu \) is the dynamic viscosity of the CH\(_4\) at a pressure of \((P_1 + P_2)/2 \, \text{(mPa-s)}\), \( L \) is the length of the anthracite sample \((\text{cm})\), \( A \) is the cross-sectional area of the anthracite sample \((\text{cm}^2)\), \( P_0 \) is the standard atmospheric pressure \((\text{MPa})\), \( P_1 \) is the methane pressure at the inlet \((\text{MPa})\), and \( P_2 \) is the methane pressure at the outlet \((\text{MPa})\). The confining pressure was set at 2 MPa, and the outlet pressure was set at atmospheric pressure. The inlet pressure was set at 0.5, 0.9, 1.5, 1.9, and 2.5 MPa, respectively. Effective stress is the difference between the confining stress and the average pore fluid pressure \[ \sigma_c = \sigma_e - \alpha P \]  

where \( \sigma_c \) is the effective stress \((\text{MPa})\), \( \sigma_e \) is the confining stress \((\text{MPa})\), \( P \) is the average pore fluid pressure \((\text{MPa})\), and \( \alpha \) is the effective stress coefficient (dimension-less, approximate to 1).

The relationship between the effective stress and confining pressure, inlet pressure, and outlet pressure is listed in Table 2. The calculation method is consistent with Li et al. \(^{75}\)

### 5.5 Image Processing

The 3D images before and after cyclical microwave modification were reconstructed to visualize and analyze the changes in the internal pore-fracture characteristics. The brightness and contrast of the images were adjusted to the appropriate ranges. Then, processes for denoising and enhancement were carried out, and edge detection and binarization segmentation were conducted. The coal matrix, minerals, and pores were divided by interactive thresholding combined with an interactive top-hat transform.

The 3D REV is a small cube that can reflect the pore structure of the whole coal sample. More petrophysical properties of coal samples can be reflected when more voxels are contained in the 3D REV. However, the selected 3D REV cannot be too large due to the limited computing capacity. Figure 12 shows the change in porosity of the cube with the change in side length (voxels) before and after cyclical microwave modification with point 1 \((800, 800, 800)\), point 2 \((1500, 1500, 1500)\), and point 3 \((2200, 2200, 2200)\) as central points. When the side length was greater than 280 voxels, the porosity tended to be a certain value and was approximately equal to the porosity of the whole sample. In this study, a cube with point 2 \((1500, 1500, 1500)\) as the center point and a side length of 500 voxels \((9.8 \, \text{mm})\) was selected as the 3D REV, as shown in Figure 13. The 3D REV was divided into 500 layers along the vertical Z-axis direction, and the porosity of each XY section was calculated to observe the internal pore structure of the 3D REV more accurately, as shown in Figure 14. The total pores and connected pores of all XY planes increased irregularly after cyclical microwave modification, which was caused by the heterogeneous distribution of molecular structures, water, and minerals in the coal.
The PNM was used to quantitatively characterize the pore and throat parameters before and after cyclical microwave modification. The PNM uses regular shapes to characterize the complex space in coal or rock. In this model, the maximal inscribed sphere algorithm was used to idealize the connected pores into two parts: pores and throats. Figure 15 shows the PNM of the 3D-REV before and after cyclical microwave modification. The calculation method was consistent with Silin and Patzek,77 Al-Kharusi and Blunt,78 Ngom et al.,79 Lin et al.,66 and Zhao et al.80

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Notes

The authors declare no competing financial interest.
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