Experimental Simulation Study on Water Migration and Methane Depressurizing Desorption Based on Nuclear Magnetic Resonance Technology: A Case Study of Middle-Rank Coals from the Panguan Syncline in the Western Guizhou Region

Junjian Zhang^{1,2,3}, Chongtao Wei^{1,2*}, Veerle Vandeginste³, Wei Ju⁴, Zengyuan Qin^{1,2}, Fangkai Quan^{1,2}, Landry Soh Tamehe^{1,5}

¹Key Laboratory of Coalbed Methane Resource & Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, China

²School of Resources and Earth Science, China University of Mining and Technology, Xuzhou 221116, China

³GeoEnergy Research Centre and School of Chemistry, University of Nottingham, University Park, NG7 2RD, Nottingham, UK

⁴Nottingham Geospatial Institute, University of Nottingham, Jubilee Campus, NG7 2TU, Nottingham, UK

⁵Department of Earth Sciences, University of Yaoundé I, P.O. Box 3412 Messa, Yaounde, Cameroon

Abstract

Water migration and methane desorption characteristics directly affect the performance of coalbed methane wells. In this paper, migration and desorption variability of methane and water in adsorption pores, seepage pores, and fractures were studied by laboratory simulation using an improved nuclear magnetic resonance displacement device. The results are as follows: Both adsorbed and bulk methane decreased logarithmically with the increase of the desorption time under the condition of one-stop desorption. The desorption process can be divided into the early rapid decline stage and the later slow desorption stage. In comparison to one-stop desorption, step-by-step depressurizing desorption can effectively increase the loss rate of the methane amount. For the two desorption modes, the variation rate of bulk methane is much higher than that of adsorbed methane at the same desorption time. The sensitivity of large pores to displacement nitrogen pressure is stronger than that of adsorption pores. In the process of methane displacement by water, the variation of bulk methane is larger than that of adsorbed methane, whereas the variation of adsorbed methane is more sensitive to injecting water pressure than that of bulk methane. The above results indicate that the quantity of water injected into the coal seam and the water drainage rate have an effect on methane desorption in the adsorption pore. Therefore, the parameters of depressurization value should be fully considered in the drainage system setting of coalbed methane wells.

1. Introduction

Coalbed methane (CBM) is one of the most important unconventional resources in China. The accumulation mechanism of coal reservoirs and the dynamic variation of physical properties during the process of drainage have attracted great attention.(1–6) However, there are relatively few studies on gas and water migration in coal reservoirs. The pressure of the coal reservoir gradually decreases to the critical desorption pressure during the drainage of CBM, which leads to methane in the adsorption pore to desorb and migrate from the matrix to the fracture by way of diffusion. Then, methane migrates and produces through fractures to the wellbore driven by the production pressure differential. Therefore, the essence of CBM drainage is the process of migration and interaction between water and methane under different pressure and temperature conditions in coal reservoirs. Methane and other gas adsorption capacities of a coal reservoir are commonly studied by an isothermal adsorption experiment(7–11) and molecular simulation methods.(12–14) Moreover, the influence of free water in a coal reservoir on methane adsorption and desorption was studied.(15–20)From the above results, it can be concluded that the adsorption capacity of methane decreases with the increase of the free water content, and the effect of free water on methane adsorption is less than that of carbon dioxide. Moreover, invasion water mainly displaces adsorbed methane in nanopores of coal and, thus, enhances the free gas content, in which the displacement mechanism can be attributed to the capillary effect and preferential flow in a coating mode.

To achieve a separate description of adsorbed and bulk methane variation, Yao et al.(21) established a set of isothermal adsorption experimental devices using low-field nuclear magnetic resonance (LF-NMR) technology. The adsorption volume decided by the devices is in good agreement with the traditional volumetric method, in which the absolute deviation between the experimental data of two methods is within $+2 \text{ m}^3/\text{t}$. This result indicates that LF-NMR can achieve an evaluation on the adsorbed methane capacity of coal. Liu et al.(22) first evaluated the exchange of adsorbed, non-adsorbed, and free-phase methane in shale reservoirs during the injection of carbon dioxide using LF-NMR technology.

The above results provide a theoretical basis for studying the characteristics of multiphase methane adsorption and migration in unconventional reservoirs. Then, Liu et al. and Yao et al. obtained the absolute adsorption isotherms of methane and divided the transverse relaxation time (T_2) value into adsorbed and free methane in shale by LF-NMR technology, respectively.(23,24) Moreover, some researchers studied the effect of different gases (carbon dioxide and nitrogen) on methane adsorption and desorption by studying the variation of T_2 spectra of multiphase methane, including adsorbed, bulk, and free methane,(25–27) and found that carbon dioxide can replace adsorbed methane from the pore surface, decreasing the adsorbed molar amount of it, and then replaced methane seems to only become a free state in the pore center and hardly escape from the organic pores.

Moreover, Liu et al.(28) simulated the one-stop desorption process of anthracite coal samples from the Qinshui basin (China) using NMR technology. This result indicates that adsorption and desorption curves of dry coal samples vary logarithmically with time, and the moisture content has a significant effect on methane adsorption and desorption.

In addition, free water inside coal reservoirs often takes part in actual CBM recovery; therefore, this factor must be considered to achieve an accurate simulation of the CBM drainage process. Some researchers characterize the stress sensitivity of the pore-fracture system by studying the variation of free water in the pore of different sizes using LF-NMR technology, which indicated that the compressibility decreases with the increase of the coal rank, and there exists a good logarithmic relationship between the value and effective stress.(29–31) Meanwhile, the migration of nitrogen, carbon dioxide, and movable water in pore–fracture systems using a T_2 spectrum was also studied,(32–34) which indicated that those gases can effectively reduce the wettability of water in the coal surface and adsorbed water can be changed to free water. Li et al.(35) studied the variation of the water content after nitrogen flooding, indicating that the retained water content of a sample with connected apertures is discharged effectively under nitrogen driving, while a sample that lacks connected apertures remains high in retained water content.

In conclusion, some achievements have been obtained in the application of NMR technology to study gas and water migration in a coal reservoir, but there are still shortcomings in terms of the experimental conditions. These are manifested in the limitation of the instrument that measures the desorption process of samples and the one-stop desorption process setting the desorption pressure to atmospheric pressure (0.1 MPa). It is difficult to objectively represent the step-by-step depressurizing in the process of CBM drainage; therefore, the results are difficult to apply directly to an actual CBM recovery project. Moreover, methane desorption and movable water migration characteristics in the one single coal sample also need further study.

In this paper, the existing nuclear magnetic displacement device and testing method were modified by adding a back-pressure valve to control desorption pressure artificially. A set of physical simulation experiments reflecting desorption of CBM during the process of pressure reduction has been conducted. The following goals were tried to achieve: Migration characteristics of free water in adsorption and seepage pores as well as fractures will be studied. Then, dynamic variation of adsorbed and bulk methane are going to be quantitatively described. Then, desorption variation of adsorbed and bulk methane under different desorption modes will be analyzed. Finally, heavy water is used as a medium to describe the methane displacement process in detail.

2. Sample and Experimental Technologies

2.1. Geological Setting and Sample Collection

The sampling area, involving two coal mines of the Tucheng area, coal mines of SJ and XZ, is located in western Guizhou, which is an important coal production base and where abundant CBM resources occur; its CBM resource is approximately between 2.20 and $2.75 \times 10^{12} \text{ m}^3$ (36) (Figure 1). Coal bearing strata are the late Permian Longtan Formation and Changxing Formation, which belong to a delta–tidal–lagoon sedimentary system, whereby the Tucheng syncline controls the general distribution of coal seams. Maturation of coal seams gradually increase with the increase of their burial depth, and the maximum vitrinite reflectance ($R_{o,max}$) is between 0.5 and 2.5%. Two fresh coal

samples (approximately $15 \times 15 \times 15 \text{ cm}^3$) were collected. Sampling location and basic parameters of the two samples are presented in Figure 1 and Table 1, respectively.

Table 1. Basic Information of Coal Samples SJ and XZ Collected from the Target Area

Sample	$R_{o,max}$ (%)	Depth (m)	Coal seam Number	Coal Mine	Proximate (wt,%)				Porosity (%)	Permeability (mD)
					M_{ad}	A_{ad}	V_{daf}	FC_{ad}		
SJ	1.32	780	12#	Shanjiao	0.88	25.04	27.71	54.19	2.07	0.47
XZ	2.20	920	7#	Xi Zhai	1.94	10.67	12.68	78.00	7.05	0.88

$R_{o,max}$, maximum vitrinite reflectance (%); M_{ad} , moisture content on an air-dried basis (%); A_{ad} , air-dried ash yield (%); V_{daf} , volatile yield on an air-dried basis (%); and FC_{ad} , fixed carbon content (%).

Figure 1

Figure 1. Distribution of the sampling locations and tectonic sketch map of the study area.

2.2. Experimental Device

The NMR simulation experiment was conducted by an improved high-temperature and high-pressure (HTHP) displacement instrument (MacroMR12-150H-1 tester). The maximum length of the sample is 150 mm. The temperature of the magnet is controlled by a nonlinear precise thermostat with a temperature range of 25 and 35 °C. ^1H resonance frequency ranges from 1 to 30 MHz. The maximum gas pressure and confining pressure of the holder are 20 and 40 MPa, respectively.

The device consists of six subsystems (Figure 2). Among them, subsystem 1 is used to display NMR signal, pressure, and temperature data. Subsystems 2 and 3 are displacement devices used to provide gas (methane and nitrogen) and water, respectively. Subsystem 4 is the key part of the whole system. It consists of a holder and a NMR device. The latter can output a continuous T_2 signal. Subsystem 5 is the pressurized portion of the instrument that can provide a continuous variation of confining pressure. Subsystem 6 is an outlet pressure controlling device, and the outlet pressure can be varied by a valve (back-pressure valve). This section is a specific modification for the tests conducted for this paper. The system can achieve a successive setting of the outlet pressure that can conduct the step-by-step depressurizing process or simulate the CBM drainage process.

Figure 2

Figure 2. Schematic of the experimental instrument.

Those parameters used in the tests include the echo interval time (0.2 ms), waiting time (1.5 s), number of echoes (5000), number of scans (64), ambient temperature (27 °C), number of iterations (10 000), and the results of the signal-to-noise ratio (SNR, 80). The Carr–Purcell–Meiboom–Gill (CPMG) sequence algorithm was used to measure the T_2 spectrum.

2.3. Experimental Methods

2.3.1. Pore Characterization

To characterize the pore–fracture system of coal samples, the pore types have been divided into adsorption pores (with a diameter smaller than 10^2 nm), seepage pores (with a diameter between 10^2 and 10^4 nm), and fractures (with a diameter larger than 10^4 nm). The above classification is according to the role of the pore in the migration and storage of CBM and the characteristics of the T_2 spectrum for different pore sizes.(37–39) The following designed tests are the focus for these three types of pores:

A total of 7–10 g of the two coal samples was selected and crushed into 2–4 mm blocks, respectively. An Autopore IV9500 mercury intrusion instrument is used for the high-pressure mercury intrusion (HPMI) porosimetry test. Each coal sample was tested for 120 pressure points; the stability time for each point was 5 s; and the working pressure of the mercury intrusion test was 0.124–270.79 MPa. For reliability of the results, data in which the pore diameter is above 10 μ m were deleted. The test results can be used to analyze the characteristics of seepage pores.

The remaining samples were further ground to 40–60 mesh to perform a low-temperature liquid nitrogen gas adsorption (LTN₂GA) test. Pore surface morphology of adsorption pores was measured using the Trostar II3020 specific surface area analyzer and pore size distribution analyzer, and the testing temperature is 77 K. The distribution and specific surface area of pores (pore diameter between 2 and 100 nm) were determined by the Barrett–Joyner–Halenda (BJH) model.(40,41) Then, a low-pressure carbon dioxide gas adsorption (LPCO₂GA) test was carried out at 273.15 K using the

Micromeritics ASAP 2020 specific surface area and pore analyzer. The distribution of micropores (pore diameter smaller than 2 nm) was determined by the density functional theory (DFT) model.(42,43)

2.3.2. Physical Simulation of Gas and Water Migration

Cylinders with a diameter of 25 mm and length of 30 mm was prepared from coal samples for NMR analyses. Two samples (SJ1 and SJ2) were drilled from coal block SJ, and one sample (XZ1) was drilled from coal block XZ. Samples SJ1 and XZ1 were used to conduct the simulation of water injection and displacement, and sample SJ2 was used to conduct the simulation of adsorption and desorption.

In the condition that the holder of the instrument is empty, the temperature of the instrument was set to 25.0 °C and the T_2 spectrum of the empty holder cavity was measured. Before the measurement, the samples were placed in a drying oven at 105 °C for approximately 6 h. After finishing it, the sample was put into the holder and then initial confining pressure of 11 MPa was set by injecting fluorine oil into the instrument. After the confining pressure stabilizes, the T_2 spectrum of the dry coal sample was measured in the same conditions as the above test.

2.3.2.1. Simulation of Water Injection and Drainage

The first step is that water injection is carried out using the apparatus shown in Figure 2. In this step, the gas (nitrogen and methane) injection system was closed and the water injection system was opened. The injecting water pressure increased from 0.6 to 6 or 8 MPa by instantly adjusting the inlet pressure to the corresponding value, and water flowing out at the outlet of valve 4 indicates that water has passed through the whole coal sample. During the whole process, the effective stress is maintained at 11 MPa by setting the value of confining pressure when the injecting water pressure varies. Lasting for 80 min, the water injection amount reached saturation under each water injecting pressure. Meanwhile, the corresponding T_2 spectrum was measured at 10 min intervals and was monitored continuously for approximately 80 min at each injecting pressure (Figure 3).

Figure 3

Figure 3. Process diagram of physical simulation experiments.

The second step is that the nitrogen flooding simulation continued to be conducted in the same sample after the water injection simulation had been completed. After 8 MPa of water pressure continuously injected into the sample for 80 min, the water injection system was closed and the nitrogen injection system was opened, whereas the rest of the operations remained the same state as the first step. The injecting nitrogen pressure increases from 1.5 MPa by instantly adjusting the inlet

pressure to the corresponding value, and it was set to 3.0 MPa at the operating time of 90 min. The T_2 spectrum is measured at 10 min intervals (Figure 3). In the whole process, the effective stress was maintained at 11 MPa by setting the value of confining pressure when the injecting water pressure changes.

2.3.2.2. Simulation of Methane Adsorption and Desorption

The dried sample was used to conduct the simulation of methane adsorption and desorption. In this procedure, the water injection system was closed, the methane injection system was opened, and the vacuum pump (2XZ-4 Rotary) pumped the instrument cavity vacuum for 1 h. The whole process consists of four steps.

The first step is the simulation of methane adsorption. Methane injecting pressure was set to 1, 2, 3, 4, 5, 6, and 7 MPa, one after the other, by instantly setting the pressure value. The T_2 spectrum of each pressure is measured by the CPMG sequence until the spectrum becomes stable (the sample is adsorbed in each injecting pressure for 2 h). In this state, the adsorption of the coal sample reaches saturation under the set pressure and the T_2 spectrum is measured at 10 min intervals.

The second step is the simulation of one-stop desorption by instantly reducing the outlet pressure to atmospheric pressure (0.1 MPa). In this step, the methane injection system was closed.

The T_2 spectrum is measured at 20 min intervals, and the total desorption time is 24 h.

The third step is the simulation of stage-by-stage depressurizing methane desorption. The one-stop desorbed sample was readsorbed to saturate the coal sample again (the measured T_2 spectrum is consistent with that of the adsorption at the first step). After adsorption saturation, the outlet of valve 4 is connected to the back-pressure valve (refer to Figure 2). The outlet pressure is reduced from 7 MPa to a lower value by quickly adjusting the value to 6, 5, 4, 3, 2, 1, and 0.5 MPa. The adjusting time interval is set to 4 h, and the T_2 spectrum is measured at 10 min intervals. To ensure consistency of time between one-stop desorption and stage-by-stage depressurizing desorption, six pressure values (the same as that of step one) were set and the measurement time of each pressure point was 4 h.

The fourth step is the simulation of methane displacement by heavy water. Heavy water is used as a medium here to study the methane displacement process because it can avoid interference between H^+ signals of methane and water. After the coal sample is desorbed for 4 h at a methane pressure of 0.5 MPa, the outlet pressure valve was removed in this step and then the water injection system was opened. The rest of the simulation system remained unchanged. The water injecting pressure increases from 1 to 3 MPa by instantly adjusting the inlet pressure to the corresponding value.

The T_2 spectrum is measured at 10 min intervals. The simulation was completed when the T_2 spectrum remain unchanged (Figure 3).

2.4. Data Selection and Processing

After the original echo data series was obtained at a specific injecting pressure and time, the data are inverted using simultaneous iterative reconstruction technique (SIRT) methods in NiumagInvert software. For this method, no user intervention is required in the data processing and complex inversion control parameters do not need to be set in advance, thereby reducing the deviation of the inversion result caused by anthropogenic factors.(44) Then, the corresponding T_2 spectrum can be obtained when the inversion process is finished. In theory, the pre-test T_2 spectrum was obtained by the superimposition T_2 spectrum of the dry coal sample and the instrument cavity (Figure 4).

The T_2 spectrum were acquired by different water and gas injection experiments. Then, the net T_2 spectrum of water and gas injection amount is the difference between the pre-test T_2 spectrum and the measured T_2 spectrum.

Figure 4

Figure 4. T_2 spectrum of dry sample SJ1.

During processing the experimental data, two methods were introduced. One is that the net T_2 spectrum of water and gas injecting amount is obtained by subtracting the pre-test T_2 spectrum from the inversed T_2 spectrum under a certain injecting pressure and time. The other is the subtraction of the pre-test data series from the measured echo data series before inversion. In comparison to the former, the T_2 spectrum obtained by the latter is relatively smoother. Therefore, the latter is used for data processing. Although the initial T_2 spectrum measured by the two methods is different, the corresponding variation of the spectrum area obtained in different T_2 values is consistent. In this paper, the dynamic process of water and gas (nitrogen and methane) injection and drainage was studied. The object of the experiment is the variation of the spectrum area under different times and pressures.

Moreover, the T_2 spectrum variations are obvious at different times under the same injecting pressure. Figure 6a is an example in which this phenomenon is explained in detail in section 3.2.1. Therefore, when studying the T_2 spectrum variation under different injecting pressures, selected data should be obtained from the saturated state under a specific pressure. On the one hand, it is a slow process for water and gases (methane and nitrogen) to saturate at a certain injecting pressure in coal reservoirs. On the other hand, the confining pressure increases accordingly with the injecting pressure variation. At the beginning of the injection, the pressure fluctuations make the measured T_2 spectrum not reflect the actual process. Therefore, the determination of the injecting time has an important effect on the results.

3. Results and Discussion

3.1. Pore Type and Pore Size Distribution

Pore type and size distributions of the two samples obtained from HPMI, LTN₂GA, and LPCO₂GA are presented in Table 2 and Figure 5. Curves of mercury injection–withdrawal and nitrogen adsorption–desorption show that the two curves of sample SJ almost coincide and they all belong to the closed curve type, implying that mercury removal efficiency is relatively higher (Table 2). This indicates that adsorption and seepage pores in the sample are dominated by open pores. In contrast, the mercury intrusive–withdrawal curves of sample XZ separate from each other, and the latter has clear

hysteresis loops and low desorption efficiency. This indicate that the seepage pores are mainly semi-closed pores and that there is a certain amount of ink bottle pores in the adsorption pores.

Table 2. Pore Volume of Samples SJ and XZ Based on HPMI, LTN₂GA, and LPCO₂GA Tests

Sample	$R_{o,max}$	Adsorption pore ($\text{cm}^3 \cdot \text{g}^{-1}$)			Seepage pore ($\text{cm}^3 \cdot \text{g}^{-1}$)			Curve type
		LP CO ₂ < 2nm	LT N ₂ 2~10 ² nm	curve type	HPMI 10 ² ~10 ³ nm	HPMI 10 ³ ~10 ⁴ nm	removal efficiency	
SJ	1.30	0.021	0.0020	Closed	0.017	0.011	72	Closed
XZ	2.20	0.062	0.0020	Opened	0.030	0.018	61	Hysteresis loop

Figure 5

Figure 5. Pore size distribution of samples SJ and XZ (a and b, pore size distributions of the seepage pore based on HPMI; c and d, pore size distributions of the adsorption pore based on LTN₂GA; e and f, pore size distributions with a diameter smaller than 2 nm based on LPCO₂GA).

From Figure 5, the total pore volume (TPV) of sample XZ is larger than that of sample SJ (TPVs of sample XZ and SJ are 0.112 and $0.051 \text{ cm}^3 \text{ g}^{-1}$, respectively); the values are relatively lower. Affected by their coal rank, the percentage of pore volume of the adsorption pore (the values are 45.1 and 57.1% , respectively) is nearly the same as that of the seepage pore. The pore volume of adsorption pores in both samples is provided by pores with a diameter of less than 2 nm , and that of the seepage pores is mainly provided by the pore diameter between 10^2 and 10^3 nm (Figure 5 and Table 2).

3.2. Water Injection and Drainage Characteristics of Three Types of Pores

3.2.1. Effect of the Injecting Pressure and Time on Water Migration

Water injection simulations were carried out according to the setup steps, as described in subsection 2.3.2.1. The purpose of this section is to analyze the variation of the movable water in the pore–fracture system under the various injecting pressures and times.

At the initial injecting pressure (0.6 MPa for 80 min) of sample XZ1, the variation of the measured net T_2 spectrum versus injection time is presented in Figure 6a. The T_2 spectral peaks gradually move to the left on the plot, reflecting that water gradually enters pores with relatively small diameters. The results also show three obvious peaks that are independent of each other, which also confirmed the results of the LPCO₂GA (LTN₂GA) and HPMI test results discussed in subsection 3.1.

Figure 6

Figure 6. T_2 spectrum variation of sample XZ1 under the same injecting pressure (0.6 MPa) (a, net T_2 spectrum variation versus injecting time; b, variation of the T_2 spectral area of total pore and adsorption pores versus injecting time; and c, variation of the T_2 spectrum area of seepage pores and fractures versus injecting time).

Panels b and c of Figure 6 show that the amount of water injected into different pores increases with increasing injecting time. For a larger aperture and smaller capillary force, the T_2 spectral area of seepage pores and fractures is higher than that of adsorption pores. The injection process of water can be clearly divided into two parts. This implies that the whole injection process can be divided into two stages, that is, the rapid injection stage (before 15 min) and the slow injection stage (after 15 min) (Figure 6c). Because water under low injecting pressure has difficulty in overcoming the high capillary force of small pores (adsorption pores), the injection rate of adsorption pores is the lowest (Figure 6b). The injecting pressure was continuously increased from 0.6 to 6 MPa following the preset procedure in subsection 2.3.2.1. Each pressure was maintained for 80 min. The T_2 spectrum variations of adsorption pores, seepage pores, and fractures are presented in Figure 7. The results indicate that the spectral area of all pores increases with increasing injecting pressure. In addition, the total spectral area of the adsorption and seepage pores has a logarithmic relationship with the injecting pressure (Figure 7).

Figure 7

Figure 7. T_2 spectrum variation of sample XZ1 under different injecting pressures (a, variation of the T_2 spectral area of total pores and adsorption pores versus injecting pressure; b, variation of the total T_2 spectral area of seepage pores and fractures versus injecting pressure).

The T_2 spectrum of adsorption and seepage pores was stable when injecting pressures reach 2.1 and 1.6 MPa, respectively. Different from the adsorption and seepage pores, water in the fractures rapidly reaches saturation when the injecting pressure is 0.6 MPa. Thereafter, the total T_2 spectral area of fractures remains unchanged as the pressure increases (Figure 7b). The injecting pressure corresponding to different pore saturation values (4, 3, and 2.1 MPa for adsorption pores, seepage pores, and fracture, respectively) indicates that water enters preferentially into fractures, followed by seepage pores and later adsorption pores (Figure 7).

3.2.2. Displacement of Water in Various Pores by High-Pressure Nitrogen Injection

To analyze the displacement effect of nitrogen on movable water in coal samples, water injection and displacement simulation of sample SJ1 was conducted following the way that was described in subsection 2.3.2.1. In the process of water injection simulation, there is no water that reaches the outlet when the injecting pressure is below 4.0 MPa. The injecting pressure of sample SJ1 corresponding to water breakthrough at the outlet is obviously higher than that of sample XZ (0.6 MPa). Shen et al.(45) and Yuan et al.(46) found that the imbibition capacity for a given sample decreases with the increase of the sample contact angle and pore tortuosity when the pore size distribution is approximately similar. Therefore, the difference of pore tortuosity and wettability between the two samples leads to this phenomenon.

After the completion of water injection simulation, nitrogen flooding simulation was conducted. Nitrogen gas was injected into water-saturated sample SJ1 at pressures of 1.5 and 3.0 MPa for 90 min, respectively. The results (Figure 8) show that the displaced water accounted for 23.4% of the total water content, indicating that nitrogen gas can effectively displace water in the sample. The process under the same displacement pressure can be divided into two parts. That is, rapid displacement in the early stage and slow displacement in the later stage (refer to Figure 8). The spectral area of adsorption pores, seepage pores, and fractures decreased significantly with

increasing displacement pressure, indicating that the displacement effect of nitrogen under higher pressure is more significant.

Figure 8

Figure 8. Spectral area of total, adsorption, and seepage pore (fracture) variation with time.

For displacement pressures of 3.0 and 1.5 MPa, the spectral area of adsorption pores, seepage pores, and fractures decreases by 10 and 60%, respectively. The results indicate that seepage pores and fractures are more sensitive to the displacement pressure than adsorption pores. The reason is that water has stronger adsorption capability than nitrogen as a wetting fluid on the surface of the adsorption pore. It is difficult for nitrogen to compete with water when it enters a micropore. Therefore, it is difficult to displace water from the adsorption pore. Moreover, it is difficult for nitrogen gas to enter an adsorption pore at a lower injecting pressure as a result of the larger capillary force in it, which leads to less displaceable water in the adsorption pore.

Nitrogen injection has become one of the important displacement technologies in the field of CBM recovery.(47–49) Results of Xue et al.(33)indicate that pressure gradients required for water displacement by nitrogen in the pore–fracture system are obviously different. The results of this subsection also show that water occurring in a large pore (seepage pore and fracture) is more sensitive to displacement of nitrogen pressure. It is common knowledge that the water content in the adsorption pore plays an important role in controlling adsorption and desorption of methane.(50,51) Therefore, displacement of water in small pores of a coal reservoir should be one of the research focuses of gas injection and displacement technology.

3.3. Adsorption and Desorption of Methane in Different Types of Pores

3.3.1. Methane Adsorption and Migration

Methane adsorption simulation of sample SJ2 was carried out according to the setup steps as described in subsection 2.3.2.2. The purpose of this simulation is to analyze the variation of adsorbed methane and bulk methane in the pore–fracture system under various methane injecting pressures.

The net T_2 spectrum of the sample at different injecting pressures for the same adsorption time (2 h) are presented in Figure 9, showing that there are three peaks in the T_2 spectrum. According to the previous NMR calibration experiments of free methane,(21,22,24) the T_2 value of smaller than 1 ms corresponds to adsorbed methane, which occurs dominantly in adsorption pores. The T_2 value that is between 10 and 100 ms corresponds to bulk methane, which is present in large pores, such as seepage pores or fractures. The T_2 value that is larger than 100 ms is the response of free methane, which exists in the space between the chamber and coal sample. Therefore, this will not be discussed in this paper.

Figure 9

Figure 9. T_2 spectrum of sample SJ2 under different methane injecting pressures.

Figure 9 shows that the spectral area of adsorbed methane is the highest among three peaks (accounting for 80% of the total spectral area approximately), indicating that adsorbed methane is the dominant form in which methane occurs. Meanwhile, Figure 10 indicates that adsorbed methane reaches saturation at a certain lower pressure, and the linear increase of bulk methane leads to the saturation of total methane at a higher pressure. This implies that the total amount of methane measured in samples that the macropore or fracture developed cannot reliably represent the adsorption characteristics of these samples.

Figure 10

Figure 10. Variation curve of adsorbed and bulk methane at different injection gas pressures.

Figure 11 shows that variation curve of adsorbed and bulk methane under the same injection gas pressure (6 MPa). At the initial stage of adsorption (before 50 min), the spectral area of adsorbed methane increases linearly with the increase of the adsorption time. Along with the continuation of the adsorption time, the adsorption rate decreases significantly and the spectral area increases slowly (after 50 min). Upon an adsorption time of 400 min, the adsorption rate of adsorbed methane tends to be stable but still not fully saturated (Figure 11a). Different from adsorbed methane, the spectral area of bulk methane increases linearly with the adsorption time. Upon an adsorption time of 250 min, the spectral area tends to be completely at equilibrium and kept stable (Figure 11b). The difference in equilibrium time is because the migration rate of adsorbed methane controlled by the Fickian law is much lower than that of bulk methane by Darcy's law.

Figure 11

Figure 11. Variation curve of adsorbed and bulk methane under the same injecting gas pressure (6 MPa).

Moreover, a similar behavior is observed under other methane injecting pressures.

3.3.2. Variation of Adsorption and Bulk Methane under One-Stop Desorption

The desorption simulation was carried out according to the setup steps in section 2.3.2.2. The purpose of this experiment is to analyze the variation of adsorbed and bulk methane with desorption time (24 h in total) under an outlet pressure equal to 0.1 MPa. Figure 12 shows that the spectral area of adsorbed and bulk methane decreases logarithmically with the increase of the desorption time.

Figure 12

Figure 12. Variation of adsorption and bulk methane under one-stop desorption.

To achieve a quantitative description of methane desorption, a phase desorption rate V is introduced to characterize methane variation per unit time. A larger value indicates a faster desorption

$$V = \frac{A_{i+1} - A_i}{30}$$

rate (1) where V is the desorption rate (p min^{-1} , where p is a unit spectral area), A_i is the total spectrum at the i measurement, and A_{i+1} is the total T_2 spectrum at the $i + 1$ measurement, with both of the variables dimensionless. Each calculation time interval is 30 min.

Figure 13a shows that the desorption process can be divided into a rapid decline (0–10 h) in the early stage and a slow desorption period (10–24 h) in the later stage. The reason for this is that the average gas content and concentration gradient are higher for samples in the early stage of desorption. With progressive gas desorption, the concentration gradient decreases, which results in the decrease of the desorption rate.

Figure 13

Figure 13. Desorption rate of adsorption and bulk methane under one-stop desorption.

Moreover, the variation rates of adsorbed and bulk methane versus desorption time were calculated (Figure 13b). The results show that the variation rate of bulk methane is much higher than that of adsorbed methane at the same desorption time (the variation rate is 38 and 68% for adsorption and bulk methane, respectively). Bulk methane directly migrates outside the sample driven by the pressure gradient, whereas adsorbed methane needs to be desorbed and converted into bulk methane under the same gradient and pass the adsorption pores by diffusion. Then, it will migrate out of the coal sample through the seepage pore or fracture by way of permeation. Therefore, the migration process of the latter is much more complicated than that of the former. Furthermore, the total variation rate of the sample is 41%, which is dominated by adsorbed methane. The main reason is that methane in coal samples mainly occurs in the adsorbed state (Figure 9).

3.3.3. Variation of Adsorption and Bulk Methane under Stage-by-Stage Depressurizing Desorption

The one-stop desorption process was carried out when the outlet pressure is atmospheric pressure (0.1 MPa), which is different from the depressurization desorption process of CBM wells. The depressurization desorption simulation was carried out as the setup steps in section 2.3.2.2. The simulation aims to reproduce the depressurization desorption process of a coal reservoir during CBM well drainage and to describe the desorption characteristics of adsorbed and bulk methane at different depressurization rates.

Figure 14 shows that the spectral area of adsorbed and bulk methane varies when the methane pressure decreases from 7 to 0.5 MPa, which illustrates that the spectrum curves of the adsorption and desorption processes do not coincide and have clear hysteresis, while the amount of bulk methane that transforms from adsorbed methane has a linear relationship with the pressure and the two curves of different processes corresponding to bulk methane are almost the same (Figure 14c). These finding can be explained by the fact that the ink bottle pores that developed in the coal sample, lead to expansion of the coal matrix in the process of methane adsorption, resulting in the narrowing of pore channels. This will lead to an increase of the force required for gas entering or leaving the pore, so that the amount of gas adsorption is greater than that of desorption.

Figure 14

Figure 14. Spectral area of adsorbed and bulk methane variation with the decrease of the outlet pressure from 7.0 to 0.5 MPa.

These indicates that the hysteresis phenomenon in the desorption process is mainly related to adsorbed methane (Figure 14b). Different from the adsorption process, the desorption data measured by NMR technology satisfy the desorption model deduced by Ma et al.(52) and do not correlate well with the Langmuir equation. The spectral area of residual total and adsorbed methane (the value is 1765 and 1056, respectively, dimensionless) can be obtained by the deduced model. The results show that about 21% of adsorbed methane has not been desorbed in specific desorption times (Figure 14b).

The spectral area variation of adsorbed and bulk methane at different depressurization stages throughout the whole desorption process (24 h of desorption) was calculated (Table_3). For the

adsorption pressure decreases from 7 to 4 MPa, the desorption of adsorbed methane is approximately 10% of the total amount. When the adsorption pressure decreases from 2.1 to 0.1 MPa, the desorption amount of adsorbed methane is 59.8% of the total desorption. Within a higher adsorption pressure, the desorption amount of adsorbed methane increases slowly compared to other lower value ranges. This indicates that the depressurizing gradient has an important effect on the desorption of adsorbed methane.

Table 3. Comparison of One-Stop Desorption and Stage-by-Stage Depressurizing Desorption (with Each Pressure Interval of 4 h)

Desorption stage	Adsorbed methane		Bulk methane		Total desorption methane	
	Desorption amount	Percentage of desorption amount /%	Desorption amount	Percentage of desorption amount /%	Desorption amount	Percentage of desorption amount /%
From 7.0 to 6.0MPa	47	1.3	62	9.9	130	3.0
From 6.0 to 5.0MPa	100	2.8	66	10.5	340	7.7
From 5.0 to 4.0MPa	250	7.1	150	23.9	300	6.8
From 4.0 to 3.0MPa	500	14.1	20	0	600	13.7
From 3.0 to 2.1MPa	529	14.9	221	35.2	697	15.9
From 2.1 to 1.2MPa	448	12.7	129	20.1	633	14.4
From 1.2 to 0.1MPa	1667	47.1	80	12.7	1694	38.6
Depressurizing desorption	3541	75.4	688	97.2	4394	73.6
One-stop desorption	1801	38.0	480	68.2	2399	41.2

The unit of desorption amount is dimensionless.

The reason is that the methane concentration of micropores in a lower adsorption pressure is smaller compared to the initial adsorption state (corresponding to the higher adsorption pressure); in this condition, the molecular distance between methane and the matrix will be larger than the equilibrium distance between them, which leads to the difficulty for methane to adsorb on the pore surface. Therefore, the conversion of adsorbed methane to free methane may increase along with the rapid decrease of the methane concentration.

Different from adsorbed methane, the variation of bulk methane under per unit pressure drop is relatively stable, and the reduction rate of them is about 12% (Table 3).

In comparison to one-stop desorption, the variation rates of adsorbed methane, bulk methane, and total methane under stage-by-stage depressurizing desorption increased by 98, 43, and 79%, respectively (Table 3). The results show that this desorption mode has a significant enhancing effect on the desorption of methane, indicating that the pressure gradient is positively correlated with the amount of methane desorbed. Therefore, it is related to the performance of CBM production wells; hence, a reasonable working system should be formulated to ensure a steady decrease of pressure difference.

3.4. Displacement of Water on Methane Desorption

After the above simulations, methane displacement by heavy water was conducted following the setup steps outlined in section 2.3.2.2. The goal of these experiments was to analyze the displacement effect of movable water on adsorbed and bulk methane.

Figure 15 shows the spectral area variation of adsorbed and bulk methane versus time under different displacement pressures. It can be seen from the figure that the spectral areas of adsorbed and bulk methane decreased by 43 and 95%, respectively, indicating that the variation of bulk methane by injected water is more significant than that of adsorbed methane. In comparison to the variation rate of bulk methane, the desorption rate of adsorbed methane increases with the increase of the displacement pressure, indicating that it is more sensitive to the displacement pressure than bulk methane. It is interpreted that different mechanisms of water on methane in two states lead to these results.

Figure 15

Figure 15. Variation of adsorbed and bulk methane versus different water pressures.

On one hand, liquid water displaces different states of methane mainly by way of volume replacement. Movable water enters into nanopores (adsorption pores) at a certain injecting pressure, which is subject to the preferential flow effect in the overlay model. Then, water flows by attachment to the pore surface to displace adsorbed methane from the nanopore surface (Figure 16). (19) With an increasing water injection rate (increasing water injecting pressure and time), the coal nanopore surface is gradually covered by water molecules, which displace more adsorbed methane and improve the displacement (Figure 15b). It is worth noting that increasing the water injecting pressure may lead to the increase of the internal pressure of ink bottle pores; therefore, bulk methane in the adsorption pores can be reattached to pore surfaces. However, the low injecting pressure in this simulation results in less water entering the semi-closed pores, which may cause the enhancing effect of water to weaken methane adsorption.

Figure 16

Figure 16. Schematic diagram for methane and water interaction in molded coal at the nanopore scale.

On the other hand, water primarily displaces bulk methane in seepage pores or fractures by external pressure. This is essentially the process by which water gradually fills the pore space. Bulk methane is displaced by volumetric displacement. However, the time effect is weaker than the pressure effect as a result of the shorter time, which indicates that the total displacement amount increases instantaneously with the increase of the pressure (Figure 15).

The above results show that water injected into a coal reservoir can displace adsorbed methane and bulk methane simultaneously. These results can provide a new reference for understanding gas and water interaction. Water invasive technology (including hydraulic fracturing technology) has been widely used in the prevention of gas outbursts in the coal mining industry CBM surface recovery. It is generally accepted that injected water mainly displaces bulk methane in the macropores and has a weak influence on adsorbed methane. Although the variation rate of adsorbed methane is relatively small compared to that of bulk methane, a considerable proportion of methane is desorbed. The difference in the effect between static water and dynamic water on methane adsorption and desorption needs further studies to better serve engineering applications.

4. Conclusion

Migration of gas and water in coal reservoirs was simulated using a modified and self-improved NMR displacement device. The injection and displacement of water, one-stop desorption, and step-by-step depressurizing desorption of the same middle-rank coal sample were conducted. Moreover, a quantitative description of the methane displacement process by water has been completed using heavy water. The conclusions are as follows: (1) For the one-stop desorption, the spectral area of adsorbed and bulk methane decreases logarithmically with the increase of the desorption time. The desorption process can be divided into the early rapid decline stage and the later slow desorption stage. Moreover, the variation rate of bulk methane is much higher than that of adsorbed methane at the same desorption time. (2) The T_2 spectrum curve of adsorption and desorption has clear hysteresis under the step-by-step depressurizing desorption, which is related to the type of pores that are adsorbed. Moreover, the variation rate of bulk methane is much higher than that of adsorbed methane. In comparison to one-stop desorption, the variation rates of adsorbed methane, bulk methane, and total methane under stage-by-stage depressurizing desorption were increased by 98, 43, and 79%, respectively. Therefore, a reasonable working system should be formulated to ensure a steady decrease of the pressure difference. (3) Nitrogen mainly displaces water in the seepage pore and fracture. The sensitivity of a large pore to displacement pressure is stronger than that of a small pore, i.e., adsorption pore. In the process of methane displacement by water, the variation rate of bulk methane is much higher than that of adsorbed methane, but the variation rate of adsorbed methane is

more sensitive to injecting water pressure than that of bulk methane. These findings are caused by the relatively strong interaction between the coal matrix and water. It is difficult for nitrogen, methane, and other gases to form competitive adsorption with water.

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