Geological Control of Irreducible Water Within the Coal Matrix and Its Quantified Evaluation Model

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ABSTRACT: This paper adopts the measurement of mercury intrusion porosimetry and nuclear magnetic resonance (NMR) to analyze the pore system and the pore structure of coal samples, and the measurement of maceral group composition, scanning electron microscopy, and energy dispersive X-ray spectroscopy to obtain the organic/inorganic composition of coal samples. Gravimetric and NMR methods are both used to calculate irreducible water saturation of the samples, and qualitative and quantitative research studies are therefore conducted. The following knowledge is obtained. Coal samples can be classified as micro-trans-pore-dominated samples, meso-macro-pore-dominated samples, cleat-dominated samples, and even development samples. The main composition of the samples is organic, and a little kaolinite and pyrite can be observed. Irreducible water saturation obtained by the gravimetric method is almost close to that gained by the NMR method. The influencing parameters can be divided into two categories. The first category contains the maximum vitrinite reflectance, volumetric factor, fixed carbon yield, volatile yield, vitrinite percentage, and inertinite percentage, which have a strong correlation with irreducible water saturation. The second category includes the buried depth and median radius, and they have a weak correlation with irreducible water saturation. Multivariate regression shows that there is a linear quaternion equation between irreducible water saturation and independent variables such as maximum vitrinite reflectance, volumetric factor, volatile yield, and vitrinite percentage.

1. INTRODUCTION

Coalbed methane (CBM) is potentially an important economic resource and has received worldwide attention as a clean and unconventional energy.1−3 Influenced by geological setting and drainage technology, CBM production is generally low in China, and the recovery efficiency in most blocks only varies from 40.0 to 54.3%.3

Geological factors influencing the recovery efficiency are maturity of organic matter, irreducible water, porosity, permeability, coal quality, gas content, reservoir pressure, and so forth.4−10 Among these factors, irreducible water is formed when water molecules are adsorbed onto solid surfaces by the capillary force and is difficult to be mobilized at lower driving pressures.10 Then, irreducible water blocks the gas inside the matrix and makes it difficult to migrate. Researches indicate that irreducible water is an important parameter influencing the CBM drainage performance,2−11 and the influence should be discussed before works of reservoir estimation, historical matching, and CBM production prediction.2,12,13

The coal matrix is made up of organic matter, clay, and others. Large amounts of nanopores developed in organic matter are the major storage space for irreducible water.13 Wang et al.14 suggest that water in different pores has different occurrence modes. Water in micropores mainly adsorbs in a monolayer type, and it is the main space for irreducible water. Water in mesopores is always in a mode of cluster, while that in macropores is almost free water. Zhou et al.15 claim that irreducible water saturation follows a normal distribution in micropores. Prammer et al.,16 Yao and Liu,17 Zou et al.,18 and Yuan et al.19 indicate that the T2 cutoff value obtained by using nuclear magnetic resonance (NMR) measurements is a measure of irreducible water saturation, with a value of about 10 ms. Combined with mercury intrusion porosimetry (MIP) measurements, Marschall et al.20 and Zhang et al.21 state that the pore system and the pore structure can influence irreducible water saturation.

Interlayer micropores formed by crystal layers in clay increase the surface area, and they can provide more space for irreducible water.2,23 This type of irreducible water is normally named clay-bound water,16,19,20 which is formed by vaporized and liquid water adsorbed onto the surface of solid particles, and it is strongly affected by the temperature and the
2. RESULTS

2.1. Sample Information. Twelve samples are collected from the underground coal mines of Qinshui basin, Shanxi Province, China, which is a sweet spot for CBM exploitation recently. The sample size is about 30 cm × 30 cm × 15 cm. The maximum vitrinite reflectance ($R_{\text{max}}$) for twelve samples ranges from 1.24 to 2.76%. Detailed information about the samples is listed in Table 1.

| sample ID | coal mine          | location           | geological time | $R_{\text{max}}$/% | buried depth/m |
|-----------|--------------------|--------------------|-----------------|-------------------|---------------|
| SIR01     | Dangdangling       | Linshi, City, Shanxi Province | C               | 1.24             | 180           |
| SIR02     | Zhenchengdi        | Gujiao City, Shanxi Province | C               | 1.32             | 300           |
| SIR03     | Malan              | Gujiao City, Shanxi Province | C               | 1.40             | 200           |
| SIR04     | Xiqu               | Gujiao City, Shanxi Province | C               | 1.49             | 255           |
| SIR05     | Tunlan             | Gujiao City, Shanxi Province | P               | 1.51             | 350           |
| SIR06     | Tunlan             | Gujiao City, Shanxi Province | C               | 1.54             | 200           |
| SIR07     | Fanshigou          | Gujiao City, Shanxi Province | P               | 1.55             | 200           |
| SIR08     | Xiqu               | Gujiao City, Shanxi Province | p               | 1.57             | 130           |
| SIR09     | Donggu             | Gujiao City, Shanxi Province | C               | 1.59             | 320           |
| SIR10     | Tunliu             | Lu’an City, Shanxi Province | P               | 2.19             | 500           |
| SIR11     | Sihe               | Jincheng City, Shanxi Province | P               | 2.72             | 430           |
| SIR12     | Chengfuchang       | Jincheng City, Shanxi Province | P               | 2.76             | 380           |

2.2. Pore Characteristic. 2.2.1. Pore Structure. MIP is always used to study the pore structure of the coal samples, and the tested parameters can be classified into three types. The first type contains parameters of median pressure, median radius, and maximum mercury penetration, which is a sign of irreducible water saturation; and identifies another factor, and neither comprehensive influence nor quantitative model has been studied. This paper adopts two methods to calculate irreducible water saturation for twelve samples collected from underground coal mines of China; analyzes the pore system, pore structure, coal quality, and organic/inorganic compositions; reveals their effects on irreducible water saturation; and finally builds a quantified evaluation model.

As a result, irreducible water is comprehensively affected by the chemical and physical properties of the pore system, pore structure, organic/inorganic components, and other external factors such as temperature, pressure, and so forth. Researches mainly focus on a single factor, and neither comprehensive influence nor quantitative model has been studied. This paper adopts two methods to calculate irreducible water saturation for twelve samples collected from underground coal mines of China; analyzes the pore system, pore structure, coal quality, and organic/inorganic compositions; reveals their effects on irreducible water saturation; and finally builds a quantified evaluation model.

clay type. Therefore, clay in the coal matrix is another space for irreducible water. As a result, irreducible water is comprehensively affected by the chemical and physical properties of the pore system, pore structure, organic/inorganic components, and other external factors such as temperature, pressure, and so forth. Researches mainly focus on a single factor, and neither comprehensive influence nor quantitative model has been studied. This paper adopts two methods to calculate irreducible water saturation for twelve samples collected from underground coal mines of China; analyzes the pore system, pore structure, coal quality, and organic/inorganic compositions; reveals their effects on irreducible water saturation; and finally builds a quantified evaluation model.

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For the first type of parameters, median pressure is another measure of median radius. A bigger median pressure corresponds to a smaller median radius, indicating that coal is dense and is not good for gas production. The median pressure varies between 206.60 and 344.43 MPa, and the median radius is from 1.80 to 3.00 nm. It shows that the coal samples are all dense. Maximum mercury penetration represents the volumetric percentage occupied by mercury. Bigger maximum mercury penetration represents more occupied pores, which is helpful for gas exploitation. The value varies from 55.92 to 79.37%, which is usually larger than 60%.

For the second type, sorting coefficient is a direct measure of sorting characteristics. A smaller sorting coefficient corresponds to a better sorting characteristic, and the value for twelve samples is between 2.75 and 4.98, indicating that the samples have a good sorting characteristic. Skewness is a measure of pore throat symmetry, and 0 means that the pore throat is exactly symmetric. The minimum value for twelve samples is −0.83, which shows that the skewness is quite good, as a similar result obtained by the sorting coefficient. Kurtosis represents the precipitous degree of frequency curves obtained.
by the MIP. If the value is 1, the frequency curve satisfies a normal distribution; if the value is above 1, the frequency curve has some peaks; and if the value is below 1, the frequency curve is much gentle. The results of kurtosis indicate that the frequency curves are generally peaky or gentle. The maximum value of kurtosis is 2.63, indicating that the pore throat is much even. Phenomena from the sorting coefficient, skewness, and kurtosis are much similar.

As for the third type of parameters, displacement pressure is the minimum pressure at which mercury starts to penetrate the coal pore, and a smaller displacement pressure corresponds to a greater pore connectivity. The value is between 0.01 and 0.18 MPa, indicating that the pore connectivity is much good. Retreat mercury efficiency is a measure of gas recovery efficiency. The value varies from 53.54 to 88.82%, which is usually higher than 60%.

2.2.2. Pore System. NMR measurements for twelve samples at the fully water-saturated and centrifuged conditions yield $T_2$ spectra shown as solid and dotted lines in Figure 1, respectively. $T_2$ distribution represents the pore size distribution, and the amplitude is a measure of pore volume.

Generally, the overlapped area of cumulative amplitudes under fully water-saturated and centrifuged conditions, and unchanged cumulative amplitudes under centrifuged conditions correspond to micro-trans-pores, meso-macro-pores, and cleats, respectively, as shown in Figure 2. As a result, volumetric proportions of three pore systems can be calculated. According to the relative volumetric proportion for each pore system, four types of coal samples can be classified, as shown in Table 3.

2.3. Coal Quality. Measurements of proximate analysis (PA) are conducted to obtain yields of moisture, ash, volatile, and fixed carbon under air-dried conditions, as shown in Table 4. Yield ranges of moisture, ash, volatiles, and fixed carbon under air-dried conditions are 0.74−2.14, 6.07−18.55, 6.11−27.55, and 57.31−82.60%, respectively.

2.4. Material Composition. Measurements of MGC are conducted to analyze the organic/inorganic compositions of the samples. As shown in Table 4, the main organic composition is vitrinite, and the range of vitrinite percentage ($P_v$) is 66.6−93.8%; the inertinite percentage ($P_i$) is relatively low, in a range of 4.8−31.8%; and no exinite can be observed. The main inorganic compositions are clay and pyrite, with relatively low ranges of 0.4−6.4 and 0.4−3.0%, respectively. Clay is developed in a shape of thin stripes (Figure 3b), and pyrite is developed in a shape of pellets (Figure 3a).
Table 3. Coal Sample Types and Their Volumetric Proportions of Pore Systems

| types                        | sample ID | micro-trans-pores/% | meso-macro-pores/% | cleats/% |
|------------------------------|-----------|---------------------|--------------------|---------|
| micro-trans-pore-dominated samples | SIR05     | 63.81               | 31.75              | 4.44    |
|                              | SIR08     | 59.55               | 26.96              | 13.49   |
|                              | SIR11     | 100.00              | 0.00               | 0.00    |
|                              | SIR12     | 96.70               | 0.00               | 3.30    |
| meso-macro-pore-dominated samples | SIR01     | 15.65               | 63.14              | 21.21   |
| cleat-dominated samples      | SIR09     | 37.00               | 62.40              | 3.46    |
| even development samples     | SIR03     | 15.91               | 15.36              | 68.73   |
|                              | SIR02     | 44.58               | 32.38              | 23.04   |
|                              | SIR04     | 17.95               | 47.75              | 34.30   |
|                              | SIR06     | 40.95               | 46.44              | 12.61   |
|                              | SIR07     | 43.92               | 31.97              | 24.11   |
|                              | SIR10     | 40.34               | 11.32              | 48.34   |

Measurements of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) are both conducted to qualitatively analyze the clay composition. Taking samples SIR10 and SIR12 as examples, the results show that the main composition is organic, and a little clay can be observed. Clay particles located at black arrows in Figures 4a,b and 4c,d are mainly lamellar or scale-like, as observed by SEM, and the EDS spectra in Figures 4c,d and 5c,d show that the main elements for the corresponding particles are C, O, Al, and Si. Therefore, the clay developed in the samples is kaolinite.

2.5. Irreducible Water Saturation.

2.5.1. Determining \( S_f \) by the Gravimetric Method. In this paper, this kind of \( S_f \) is defined as \( S_{\text{ir}g} \). The calculated \( S_{\text{ir}g} \) varies between 27.00% (sample SIR03) and 91.58% (sample SIR11), which is usually higher than 50%.

2.5.2. Determining \( S_f \) by the NMR Method. Based on NMR experiments, \( S_f \) determined by the NMR method is listed in Table 5. In this paper, this kind of \( S_f \) is defined as \( S_{\text{ir}g} \). \( S_{\text{ir}g} \) has a wide range, with the lowest value of 28.67% for the sample SIR03 and the highest value of 92.85% for the sample SIR11.

Table 4. Proximate Analysis and Maceral Group Composition for Coal Samples

| sample ID | proximate analysis/% | maceral group composition/% |
|-----------|----------------------|-----------------------------|
|           | \( M_{\text{ad}} \) | \( V_{\text{ad}} \) | \( A_{\text{ad}} \) | \( FC_{\text{ad}} \) | organic | inorganic | \( P_v \) | \( P_i \) | clay | pyrite | \( R_{\text{max}} \) % |
| SIR01     | 0.86                 | 16.85                       | 10.11                       | 72.18                       | 66.6 | 31.8 | 0.4 | 1.2 | 1.24 |
| SIR02     | 0.66                 | 27.55                       | 14.48                       | 57.31                       | 81.0 | 10.0 | 2.0 | 1.0 | 1.32 |
| SIR03     | 0.76                 | 21.92                       | 14.60                       | 62.72                       | 66.8 | 30.4 | 2.2 | 0.6 | 1.40 |
| SIR04     | 0.98                 | 23.63                       | 14.55                       | 60.83                       | 82.2 | 13.8 | 1.2 | 2.8 | 1.49 |
| SIR05     | 0.76                 | 19.18                       | 10.55                       | 69.51                       | 72.0 | 24.8 | 1.6 | 1.6 | 1.51 |
| SIR06     | 0.74                 | 18.17                       | 6.61                        | 74.48                       | 75.4 | 17.2 | 4.4 | 3.0 | 1.54 |
| SIR07     | 0.75                 | 19.39                       | 6.07                        | 73.79                       | 71.0 | 21.6 | 3.4 | 1.2 | 1.55 |
| SIR08     | 0.84                 | 16.36                       | 15.25                       | 67.56                       | 85.0 | 10.0 | 4.4 | 0.6 | 1.57 |
| SIR09     | 0.83                 | 16.63                       | 18.55                       | 63.99                       | 74.4 | 22.0 | 1.8 | 1.8 | 1.59 |
| SIR10     | 0.94                 | 9.95                        | 9.51                        | 79.59                       | 83.8 | 6.4  | 6.4 | 0.4 | 2.19 |
| SIR11     | 1.14                 | 6.11                        | 10.15                       | 82.60                       | 93.8 | 4.8  | 1.6 | 1.2 | 2.72 |
| SIR12     | 2.14                 | 7.45                        | 10.99                       | 79.42                       | 93.4 | 5.0  | 1.2 | 0.4 | 2.76 |

\( M_{\text{ad}} \) - air-dried moisture yield; \( V_{\text{ad}} \) - air-dried volatile yield; \( A_{\text{ad}} \) - air-dried ash yield; \( FC_{\text{ad}} \) - air-dried fixed carbon yield; \( P_v \) - vitrinite percentage; \( P_i \) - inertinite percentage.

2.5.3. Final \( S_f \). Difference percentage is adopted in this paper to quantitatively describe the difference between \( S_{\text{ir}n} \) and \( S_{\text{ir}g} \), which is expressed as follows

\[
P_d = \left[ \frac{S_{\text{ir}n} - S_{\text{ir}g}}{S_{\text{ir}n}} \right] \times 100\%
\]

where \( P_d \) is the difference percentage, %.

Figure 6 and Table 5 show the comparison between \( S_{\text{ir}n} \) and \( S_{\text{ir}g} \). Excluding samples SIR04 and SIR10, \( S_{\text{ir}n} \) is close to \( S_{\text{ir}g} \) for the rest of the samples, with \( P_d \) lower than 10%. As a result, the two methods are generally reliable, and \( P_d \) may have resulted from experimental errors for different experiments. The final \( S_f \) is calculated by the arithmetical average of \( S_{\text{ir}n} \) and \( S_{\text{ir}g} \) as shown in Table 5, which can reduce the errors caused by different experiments.

3. DISCUSSION

3.1. Geological Influence on Irreducible Water Saturation.

3.1.1. Influence of Buried Depth and \( R_{\text{max}} \) on \( S_f \). Regressive analysis of buried depth versus \( S_f \) shows that there is a positive relationship between them, but the trend line type is indeterminate, as shown in Figure 7. Buried depth reflects the geographical location of the coal reservoir, which is a measure of overburden pressure. A bigger buried depth will always receive a higher reservoir pressure, which makes the coal matrix dense and results in a higher irreducible water saturation. Regressive analysis of \( R_{\text{max}} \) and \( S_f \) shows that it has a positively linear relationship, as shown in Figure 7. \( R_{\text{max}} \) is an important index for coalification. The increase of \( R_{\text{max}} \) will increase the volumetric proportion of micro-trans-pores and lead to the increase of irreducible water saturation.

3.1.2. Influence of Pore Features on \( S_f \). Pore size is the main index of pore features, which can be reflected by the median radius measured by MIP. Regressive analysis of median radius versus \( S_f \) is conducted, as shown in Figure 8, and it indicates that there is a slightly negative correlation. Another index for pore feature is volumetric percentages of three pore systems. As studied preliminarily, most of the irreducible water is stored in micro-trans pores, some occurs in meso-macro pores, while a few in cleats. To highlight the influence of micro-trans pores on irreducible water saturation,
Volumetric factor is defined in this paper, which is expressed as follows

\[ V_f = \frac{(V_2 + V_3)}{V_1} \]  \hspace{1cm} (2)

in which \( V_f \) is the volumetric factor; \( V_1 \) is the volumetric percentage of micro-trans-pores; \( V_2 \) is the volumetric percentage of meso-macro-pores; and \( V_3 \) is the volumetric percentage of cleats.

Regressive analysis of \( V_f \) and \( S_{ir} \) is conducted as shown in Figure 8. It indicates that there is a strongly negative correlation between them.

The above two negative correlations both reveal and prove the result that micro-trans-pores are the main space for irreducible water, as studied in ref 14.

### 3.1.3. Influence of Coal Quality on \( S_{ir} \)

Regressive analyses of \( S_{ir} \) versus \( FC_{ad}/V_{ad} \) are conducted as shown in Figure 9. \( S_{ir} \) has a strongly positive relationship with \( FC_{ad} \), while a negative correlation with \( V_{ad} \). \( V_{ad} \) is a very important index for both coal classification and coalification, which has a strongly negative correlation with \( R_{o,max} \). Then, a negative correlation between \( V_{ad} \) and \( S_{ir} \) can be found. \( FC_{ad} \) is an indirect parameter which is calculated by using one hundred minus the total of \( V_{ad} \), \( A_{ad} \), and \( M_{ad} \). Therefore, \( FC_{ad} \) has a negative correlation with \( V_{ad} \) and a positive correlation with \( S_{ir} \).

### 3.1.4. Influence of Material Composition on \( S_{ir} \)

Regressive analyses of \( S_{ir} \) and parameters obtained by MGC measurements are conducted, as shown in Figure 10. It can be seen that \( P_v \) has a positively linear relationship with \( S_{ir} \), whereas \( P_i \) decreases. As a result, \( S_{ir} \) has a positive relationship with \( P_v \) whereas a negative relationship with \( P_i \). The content of clay is quite low and the type is single for all the samples, so the influence of clay on irreducible water saturation is neglected here.

### 3.2. Quantified Evaluation Model

On the basis of the influenced degrees, parameters in section 3.1 can be divided into two categories. The first category is the strongly influencing parameters, including \( R_{o,max} \), \( V_f \), \( FC_{ad} \), \( V_{ad} \), \( P_v \), and \( P_i \). This category of parameter has a strong correlation with \( S_{ir} \), and the regressive analyses show that the correlation coefficients are generally higher than 0.5. The second category is the weakly influencing parameters, containing the buried depth and the median radius. This category of parameter has a weak or none correlation with \( S_{ir} \), and the correlation coefficients are quite low. Before modeling, the weakly influencing parameters are...
eliminated, and only strongly influencing parameters are adopted as independent variables. Among all independent variables, both $\text{FC}_{\text{ad}}$ and $V_{\text{ad}}$ describe the coal quality, and $\text{FC}_{\text{ad}}$ is an indirect parameter which is calculated by using other parameters tested from PA measurements. Therefore, only $V_{\text{ad}}$ is considered as the independent variable. Similarly, $P_v$ and $P_i$ both describe the MCG measurement, and they two have a strong correlation. Then, only $P_v$ is chosen as the independent variable.

In conclusion, the final independent variables are $\text{Ro}_{\max}$, $V_f$, $V_{\text{ad}}$, and $P_v$. Among these four variables, $\text{Ro}_{\max}$ reflects the coalification degree, $V_f$ is a measure of the pore system, $V_{\text{ad}}$ measures the coal quality, and $P_v$ represents the material composition. Multivariate regression is adopted here to quantified evaluation of irreducible water saturation, and the result is displayed as eq 3, with a fitting degree of 0.89.

$$S_{ir} = -11.456 \text{ Ro}_{\max} - 3.214 V_f - 1.775 V_{\text{ad}} + 0.588 P_v + 66.727$$

where $S_{ir}$ is the irreducible water saturation; $\text{Ro}_{\max}$ is the maximum vitrinite reflectance; $V_f$ is the volumetric factor; $V_{\text{ad}}$ is the air-dried volatile yield; and $P_v$ is the vitrinite percentage.

This quantified evaluation is helpful to better understand the microgeological characteristics and the geological influences on irreversible water saturation.

**Table 5. Irreducible Water Saturation Gained by the Gravimetric Method and the NMR Method**

| sample ID | $L$/cm | $\varphi$/cm | $m_s$/g | $m_f$/g | $S_{ir}$/% | $A_c$ | $A_f$ | $S_{ir}$/% | $P_{d}$/% | $S_{ir}$/% |
|-----------|--------|-------------|--------|--------|----------|------|------|----------|---------|---------|
| SIR01     | 3.18   | 2.52        | 20.37  | 21.09  | 20.75    | 52.78 |      | 435.51  | 734.51  | 59.29   |
| SIR02     | 3.41   | 2.50        | 14.24  | 20.22  | 17.33    | 51.67 |      | 1140.31 | 2129.89 | 53.54   |
| SIR03     | 3.52   | 2.48        | 14.56  | 20.67  | 16.21    | 27.00 |      | 414.00  | 1444.01 | 28.67   |
| SIR04     | 3.16   | 2.51        | 20.46  | 21.28  | 20.74    | 34.15 |      | 579.62  | 1272.34 | 45.56   |
| SIR05     | 2.56   | 2.50        | 20.34  | 21.25  | 20.90    | 61.54 |      | 1251.21 | 2004.40 | 62.42   |
| SIR06     | 3.52   | 2.49        | 15.36  | 21.28  | 18.45    | 52.20 |      | 1408.50 | 2611.55 | 53.93   |
| SIR07     | 2.55   | 2.48        | 16.12  | 20.12  | 18.21    | 52.25 |      | 813.79  | 1555.69 | 52.31   |
| SIR08     | 2.54   | 2.50        | 21.32  | 23.32  | 22.52    | 60.00 |      | 824.01  | 1293.78 | 63.69   |
| SIR09     | 2.52   | 2.50        | 16.25  | 21.12  | 18.65    | 49.28 |      | 429.32  | 859.39  | 49.96   |
| SIR10     | 3.15   | 2.51        | 20.73  | 21.44  | 21.09    | 50.70 |      | 234.89  | 339.05  | 52.31   |
| SIR11     | 3.30   | 2.53        | 15.65  | 21.47  | 20.98    | 91.58 |      | 2022.16 | 2177.82 | 92.85   |
| SIR12     | 3.19   | 2.51        | 21.74  | 22.65  | 22.36    | 68.13 |      | 1336.73 | 1715.95 | 77.90   |

$L$ = length; $\varphi$ = diameter; $m_s$ = dried weight; $m_f$ = weight of the fully water-saturated sample; $m_c$ = weight of the centrifuged water sample; $S_{ir}$ = irreducible water saturation gained by the gravimetric method; $s_{ir}$ = irreducible water saturation gained by the NMR method; $P_{d}$ = difference percentage.
4. CONCLUSIONS

This paper measures the pore system, pore structure, coal quality, and organic/inorganic compositions of the coal samples; qualitatively analyzes their influences on irreducible water saturation; and finally builds a quantified evaluation model. Some findings are achieved.

Twelve coal samples are classified as micro-trans-pore-dominated samples, meso-macro-pore-dominated samples, cleat-dominated samples, and even development samples based on the relative volumetric percentage of each pore system. Measurements of SEM and EDS indicate that the main composition of the samples is organic, and a little lamellar or scale-like kaolinite and pyrite in the shape of pellets can be observed.

Irreducible water saturation calculated by the gravimetric method is close to that gained by the NMR method, and the difference percentage is lower than 10%. The arithmetical average is adopted as the final irreducible water saturation, in the range of 27.84−92.22%.

Influencing parameters can be divided into two categories. The first category contains $R_{o,max}$, $V_o$, $FC_{sh}$, $V_{sh}$, $P_v$, and $P_o$, which have a strong correlation with $S_i$. The second category includes the buried depth and median radius, and they have a weak correlation with $S_i$. Multivariate regression shows that there is a linear quaternion equation between $S_i$ and independent variables of $R_{o,max}$, $V_o$, $V_{sh}$, and $P_o$, which helps to better understand the geological influence of reservoir parameters on irreducible water.

5. EXPERIMENTAL SECTION

Three kinds of samples are prepared in this paper. The first kind is cylinder samples with a diameter of 25 mm and a height of 30−50 mm, and they are used for NMR measurements. The second kind is block samples with a length of about 30 mm, which will be further processed for measurements of MIP, maceral group composition (MGC), SEM, and EDS. The third kind is powder samples, and they are used for PA.

5.1. Gravimetric Method. The gravimetric method can be used to calculate irreducible water saturation for coal samples. Weights of dried samples, fully water-saturated samples, and centrifuged samples are all measured, and the gravimetric method is expressed as follows

$$S_{ir} = \left( \frac{m_c - m_d}{m_f - m_d} \right) \times 100\%$$

where $m_c$ is the weight of centrifuged samples, in g; $m_d$ is the weight of dried samples, in g; $m_f$ is the weight of fully water-saturated samples, in g; and $S_{ir}$ is the irreducible water saturation, in %.

5.2. NMR Method. Combined with NMR measurements, the NMR method can also be used to determine irreducible water saturation. Kenyon,\textsuperscript{30} Kleinberg,\textsuperscript{31} Yao et al.,\textsuperscript{32,33} and Li et al.\textsuperscript{34} describe the detailed theory of NMR measurements, which establishes a linear relationship between the pore radius and the NMR signal, given by

$$1/T_2 = \rho_2 (S/V)$$

where $T_2$ is the transverse relaxation time that resulted from surface interactions; $\rho_2$ is the constant that represents the transverse relaxation strength; and $S/V$ is the surface to volume ratio related to pore radius.

Measurements are conducted under two conditions. One is the fully water-saturated condition, which is used to analyze the pore system and the pore size. The other one is the centrifuged condition, and is used to determine the irreducible water. During measurements, the related parameters were set as follows: magnetic field strength, 1200 G; resonance frequency, 2.38 MHz; echo spacing, 0.6 ms; waiting time, 5 s; echo numbers, 2048; and numbers of scans, 64.

After measurements, irreducible water saturation determined by the NMR method can be obtained, and it equals the ratio of spectral areas in the centrifuged condition and the fully water-saturated condition.

5.3. Pore Structure and Pore System. MIP for block samples is performed. The measurements run up to a pressure...
of $6 \times 10^4$ Psia, indicating that pore diameters as small as 3 nm are penetrated. MIP aims to obtain the pore size, pore connectivity, and sorting characteristic of the coal samples.\textsuperscript{35,36} $T_2$ spectra obtained by NMR measurements in the fully water-saturated condition are obtained in this paper, which aims to classify the coal pore system and calculate the volumetric proportion of each pore system, as described in detail in ref 35.

5.4. Material Composition and Coal Quality. PA is conducted to obtain the coal quality of the samples by following the Chinese Standard (GB/T) 212-2008. MGC, SEM, and EDS are performed to analyze the organic/inorganic compositions of the coal samples. MGC is measured following the Chinese Oil and Gas Industry Standard (SY/T) 6414-2014, and is used to analyze the organic compositions.\textsuperscript{37,38} SEM and EDS aim to analyze the inorganic compositions, and the related parameters are set as follows: detected area, 10 mm$^2$; maximum input count, 1,000,000 cps; maximum output count, 400,000 cps; and element range: Be−Am.

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Notes
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