Petrophysical characterization of coals by low-field nuclear magnetic resonance (NMR)

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Abstract
Nuclear magnetic resonance (NMR) has been widely used in petrophysical characterization of sandstones and carbonates, but little attention has been paid in the use of this technique to study petrophysical properties of coals, which is essential for evaluating coalbed methane reservoir. In this study, two sets of NMR experiments were designed to study the pore types, pore structures, porosity and permeability of coals. Results show that NMR transverse relaxation ($T_2$) distributions strongly relate to the coal pore structure and coal rank. Three $T_2$ spectrum peaks identified by the relaxation time at 0.5–2.5 ms, 20–50 ms and >100 ms correspond to pores of <0.1 $\mu$m, >0.1 $\mu$m and cleats, respectively, which is consistent with results from computed tomography scan and mercury intrusion porosimetry. Based on calculated producible and irreducible porosities through a $T_2$ cutoff time method, we propose a new NMR-based permeability model that better estimates the permeability of coals. In combination with mercury intrusion porosimetry, we also propose a NMR-based pore structure model that efficiently estimates the pore size distribution of coals. The new experiments and modeling prove the applicability of NMR in petrophysical characterization of intact coal samples, which has potential applications for NMR well logging in coalbed methane exploration.

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1. Introduction

Nuclear magnetic resonance (NMR) provides a fast, convenient and nondestructive tool for characterizing complex porous media, particularly the petroleum reservoir rocks. In the 1960–1980s, a low-field $^1$H proton magnetic resonance relaxation method was widely used for petrophysical analysis and well logging in petroleum exploration [1–3]. Since 1990s, this method has become an indispensable tool for characterizing reservoir properties such as porosity, permeability, viscosity and saturation of oil and gas [4–12].

Coal is a special porous media that serves as a type of unconventional gas reservoir for coalbed methane (CBM) and has physical properties similar to some of the petroleum reservoirs. Thus, it is possible to apply the NMR relaxation method to characterize coal reservoir properties. However, existing applications of solid-state proton ($^{13}$C and $^1$H) NMR to coals mostly focused on coal molecular structure [13–15], coal type and rank [16], coal composition [17,18], or fluid migration in coals [19,20]. Little attention has been devoted to the use of liquid-state $^1$H NMR to study the petrophysical properties of coals, which is essential for CBM reservoir evaluation.

Existing methods for studying petrophysical properties of coals include mercury intrusion porosimetry (MIP), gas adsorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and small angle scattering techniques (SAS) [21–23]. However, all these methods have limitations on the data quality or require sample destruction. For MIP, high-pressure intrusion by mercury may either distort the skeletal porous structure of samples [24] or reduce the amount of large pores due to the shielding effects of smaller pores [25]. Gas adsorption can only obtain information about the micro- and mesopores of coals and require sample destruction [26]. Microscopic techniques (e.g. SEM, TEM and SAS) can only provide local pictures of a sample [27]. Hence, there is a need to seek for a new method that can integrate the petrophysical properties of intact coal samples to better evaluate the quality of coalbed methane reservoir.

In this paper, we present the experimental results of low-field NMR relaxation of coal samples. The results indicate capabilities of NMR in characterizing coal porosity, pore geometry, pore connectivity, and permeability. The advantages of the NMR technique include that it does not destroy the sample and it is less time-consuming. Moreover, the NMR technique uses a portable instrument that is convenient to be used in the field. These advantages are important for CBM exploration, logging of coalfields, and subsequent laboratory analysis of core samples.
2. Experimental methods

2.1. Samples

Eleven coal samples were collected from underground mines of the Qinshui basin, the Ordos basin, and the Hongyang coalfield, China. All samples were carefully packed and then immediately sent to the laboratory for experiments. For each sample, one or more horizontal cylindrical core plugs (2.5 cm in diameter) were cut parallel to the bedding planes.

These core plugs and core cuttings from the end or bottom of the plugs were used for experiments. The core plugs were performed for helium porosity, air permeability, water-saturated porosity and NMR measurements, and for MIP and CT scan analyses. The core cuttings were used for vitrinite reflectance measurements and maceral analyses following the Chinese standard GB/T 6948-1998.

2.2. Porosity and permeability analyses

The helium porosity \( q_h \) and air permeability \( K_a \) were measured using the routine core analysis methods by the Chinese Oil and Gas Industry Standard (SY/T 5336-1996). The measurements were under simulated in situ stress conditions using a tri-axial cell with isotropic ambient pressure of 2.5 MPa. The porosity was measured using the helium expansion method and the absolute permeability was determined using a bubble flowmeter by flowing air through the core sample until the variation of permeability becomes relatively stable.

Water porosity \( \phi_w \) analysis was performed by a gravimetric method for most of the samples except for HC3-5, which was broken and could not be measured at saturation. The core samples were dried at 80 °C for at least 24 h in a vacuum oven. After bulk volumes and weights were measured and dry densities of the samples were calculated, these samples were saturated with 100% distilled water for at least another 24 h. Then bulk volumes and weights were remeasured, and wet densities were calculated. Finally, the water porosities of the samples were calculated by the values of dry and wet densities.

2.3. NMR measurements

Following the water porosity analysis, two sets of NMR measurements were performed: one at 100% water-saturated condition \( (S_w) \) and another at an irreducible water condition \( (S_i) \). All core plugs were performed for NMR measurement at \( S_w \). Samples were then centrifuged using a PC-1 Petroleum Core Centrifuge to obtain a perfect irreducible water condition at a centrifuge capillary pressure of 1.4 MPa [28]. Nine selected samples were performed for NMR measurement at \( S_i \).

The NMR measurements were conducted using a Rec Core 2500 instrument manufactured by the China National Petroleum Corporation. The instrument has a constant magnetic field strength of 1200 gauss and a resonance frequency of 2.38 MHz. The measurement parameters were set as follows: echo spacing, 0.6 ms; waiting time, 5 s; echo numbers, 2048; numbers of scans, 64. After the measurements, transverse relaxation time \( (T_2) \) distributions were computed by multi-exponential inversion of the echo data with 51 preset decay times logarithmically spaced from 0.1 ms to 10 s [8].

2.4. CT scans and MIP measurements

After the NMR experiments, the core samples were immediately dried for computed tomography (CT) scans. The details about the CT scans were discussed elsewhere [29]. Following the CT scans, seven of the twelve core samples were analyzed for MIP.

The MIP was performed using an Autopore III 9420 Instrument (Micrometrics, USA) by the SY/T 5346-2005. The MIP measurements run up to a pressure of 32 MPa, meaning that pore throats as small as 0.02 μm were penetrated. Mercury intrusion/withdrawal curves were measured and used to generate the pore size distributions. The purpose of performing CT scans and MIP is to verify the pore size distribution results obtained by NMR.

3. Results

3.1. Characteristics of the coal samples

The selected samples represent a wide range of coals in coal rank, porosity, and permeability (Table 1). They vary from sub-bituminous to anthracite with mean maximum vitrinite reflectance in oil \( (R_o) \) of 0.39–3.57%. The porosities \( (\phi_w) \) of these samples range from 1.56% to 9.00%, with a mean of 4.56%. Their permeabilities \( (K_a) \) are quite diverse. The highest permeability is 82.1 mD from sample HC3-5, followed by 14.9 mD from G2. The moderate permeabilities are 3.09 and 1.20 mD from WL7 and XIM12, respectively. The permeabilities of other samples are commonly <0.1 mD.

<table>
<thead>
<tr>
<th>Sample *</th>
<th>Coal basin</th>
<th>( R_o ) b (%)</th>
<th>( \phi_v ) c (%)</th>
<th>( \phi_I ) c (%)</th>
<th>( \phi_d ) c (%)</th>
<th>MM d (%)</th>
<th>( \phi_w ) e (%)</th>
<th>( \phi_a ) e (%)</th>
<th>( K_a ) f (mD)</th>
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<tr>
<td>HC3-5</td>
<td>Ordos</td>
<td>0.39</td>
<td>55.1</td>
<td>37.2</td>
<td>6.8</td>
<td>0.9</td>
<td>6.70</td>
<td>-</td>
<td>82.1</td>
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<td>LINS</td>
<td>Hongyang</td>
<td>0.8</td>
<td>78.5</td>
<td>17.5</td>
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<td>0.4</td>
<td>2.27</td>
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<td>69.8</td>
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<td>0.1</td>
<td>5.20</td>
<td>3.21</td>
<td>3.09</td>
</tr>
<tr>
<td>STJ1-10</td>
<td>Ordos</td>
<td>1.56</td>
<td>82.3</td>
<td>9.5</td>
<td>0</td>
<td>8.2</td>
<td>2.30</td>
<td>0.85</td>
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<td>YQ2X15-1A</td>
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<td>76.6</td>
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<td>89.6</td>
<td>10.4</td>
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<td>1.74</td>
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<td>2.42</td>
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<td>0.6</td>
<td>1.56</td>
<td>1.03</td>
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</tr>
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</table>

* Sample HC3-5 is broken and failed for \( \phi_w \) measurement at water saturation.

b Mean maximum vitrinite reflectance in oil.

c \( V \), \( I \), and \( L \) represent the volume percentages of vitrinite, inertinite and liptinite in coal maceral composition, respectively. MM is the volume percentage of minerals on dry basis.

d \( \phi_v \) and \( \phi_d \) are porosities measured by helium gas injection and water-saturated methods.

e Air permeability.

References:

[28] [29]
Samples YQ2K15-1 and YQ2K15-2 are subsamples cut from the same coal block. They are used to test the heterogeneity of this coal and to prove the reproducibility of the NMR measurements.

3.2. NMR relaxation time distributions of coals

3.2.1. Low-field NMR relaxation

Theoretically, a NMR measurement consists of using an external magnetic field to align hydrogen magnetic moments, and creating a dipole moment in the hydrogenous fluid component of the sample. The amplitude of the dipole moment is proportional to the number of hydrogen atoms present and thus, is a measure of the pore volume filled with fluid. The dipole moment time evolution can be decomposed into a spectrum of attenuation times, i.e., the longitudinal ($T_1$) and transverse ($T_2$) relaxation time distributions.

The measurement of $T_2$ relaxation is preferred as it is fast and usually provides similar distribution to $T_1$ [5,30]. For low frequency and short pulse spacing, $T_2$ carries the same pore information as $T_1$.

The drawback of $T_2$ is that it is more complicated to interpret as three possible relaxation mechanisms (i.e. the bulk, diffusion, and surface relaxations) can occur. Diffusion relaxation can be reduced when a low and uniform magnetic field and a short pulse spacing is used. In addition, bulk relaxation can also be reduced because of nonviscous water inside nonmagnetic coal samples [1,4,7,31]. Thus, the NMR $T_2$ relaxation examined in this study is mainly attributed to surface relaxation, which occurs at the interface between water and coal. Surface relaxation is a function of the surface to volume ratio of pores [4,6]:

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

where $T_2$ is the transverse relaxation time resulting from surface interactions; and $\rho_2$ is a constant representing the transverse
relaxation strength. $S/V$ is the surface to volume ratio that relates to the pore size.

Since smaller pores have high $S/V$ value, Eq. (1) shows that hydrogen proton in smaller pores relax faster than that in larger pores [28,30]. Consequently, the $T_2$ distribution in core samples reflects the pore size distribution, with the smallest pores having the shortest relaxation time and the largest pores having the longest relaxation time.

3.2.2. NMR $T_2$ distribution at $S_w$

The NMR measurements at $S_w$ were performed for the 12 coals. Each NMR measurement yields a NMR $T_2$ spectrum at $S_w$. These $T_2$ spectra at $S_w$ are shown as gray solid lines in Fig. 1. Compared with the typical unimodal or bimodal distribution of sandstones [8,9], the $T_2$ spectra distribution of the selected coals commonly show three peaks, i.e. the p1 at 0.5–2.5 ms, p2 at 20–50 ms and p3 at >100 ms (Fig. 1a, c, g, h and j). The p1 is present in all samples. In contrast, the p2 and p3 are not found in some samples (Fig. 1e, f, i and l), and in some samples they are found to be combined together as a new peak (p2+p3) (Fig. 1b, d and k).

It seems that the fully saturated $T_2$ distribution depends on coal ranks. The $T_2$ distributions can be divided into four groups based on the shape of p1 and p2, and the coal rank of the selected coals. The first group (Group 1) is the sub-bituminous HC3-5 with $R_o$ of 0.39%. For HC3-5, the peaks of p1 and p2 are obvious, and the amplitude of p1 is higher than that of p2. The second group (Group 2) includes a high volatile bituminous (LUNSA) and two medium volatile bituminous (WL7 and STJ1-10), with $R_o$ of 0.8–1.56%. For Group 2, the amplitude of p1 is commonly lower than that of p2. The third group (Group 3) includes two low volatile bituminous coals (YQ2K15-1 and YQ2K15-2), two semi-anthracites (YQ1K-3 and YQ3K-3) and three anthracites (SH3, XIM 12 and CZ3), with $R_o$ of 1.87–3.57%. Group 3 commonly has a distinct peak of p1 at $T_2$ value of ~1 ms (Fig. 1e–j and l), and a very small peak of p2. The last group is the G2 with $R_o$ of 2.7%. G2 has small amplitude of p1, but large amplitude of p2+p3 at the $T_2$ value of ~70 ms (Fig. 1k). G2 was collected adjacent to a dike, where the magma contact metamorphism may have induced a change in the pore structure, leading to the generation of macropores in the coal.

For the selected coals, it seems that the dominating $T_2$ spectrum peak coincides with the large relaxation time area for low-medium rank coals (Fig. 1a–d); whereas the $T_2$ peak covers small relaxation time area for high rank coal (Fig. 1e–l).

Fig. 1e and f shows the $T_2$ distributions of the two subsamples from the same coal sample block. Their $T_2$ distributions are very similar in $T_2$ morphology and amplitude, confirming the reproducibility of the NMR measurements.

3.2.3. NMR $T_2$ distribution at $S_w$

The definition of irreducible water condition ($S_w$) is important. In this study, the $S_w$ relates to the results of centrifuging experiment. The centrifuging is to expel free water within connective macropores, and theoretically it is based on the Washburn equation:

$$r_c = \frac{-2\sigma \cos \theta}{P_c}$$

where $P_c$ is the centrifuging pressure in MPa; $r_c$ is the minimal pore radius (μm) for water to discharge at the pressure $P_c$; $\theta$ is the contact angle between water molecule and pore surface; and $\sigma$ is the interfacial tension of coal and water.

Although the $\theta$ and $\sigma$ of coal-to-water vary with samples [32], for simplification purpose, they were assigned with values of 0.076 N/m and 60°, respectively, according to the study by Fu et al. [33]. As a result, Eq. (2) becomes

$$r_c = \frac{0.14}{P_c}$$

From Eq. (3), it becomes obvious that the pore radius ($r_c$) for water to discharge relates to the centrifuging pressure ($P_c$). The centrifuge pressure of 1.4 MPa used in the experiment corresponds to a pore radius of ~0.1 μm. This means that the minimum pore throat size for the water to be centrifuged is about 0.1 μm. In other words, the irreducible water is defined as including not only the clay-bounded water, but also the water left in the pores <0.1 μm.

The NMR measurements at $S_w$ were only performed for nine coals. Their $T_2$ spectra are shown as dark dashed lines in Fig. 1b–e, h–l. The $T_2$ spectrum at $S_w$ is commonly lower than that at $S_w$, except for STJ1-10. In terms of the three peaks, the p1 at $S_w$ shows very small difference with that at $S_w$, but the p2 at $S_w$ is distinctly smaller than that at $S_w$. The p3 is commonly not distinguishable at $S_w$. For each coal, the difference in the $T_2$ distributions at $S_w$ and $S_w$ depends on the pore structure of coals, which will be discussed later.

4. Discussion

As a tool for core analysis or well logging, NMR relaxation has been successfully used to determine the physical properties of traditional petroleum reservoirs. However, as the CBM reservoir, coal is different from both sandstones and carbonates. To explore the potential of applying NMR relaxation to coal reservoir characterization, this section will discuss how NMR relaxation can be used as an independent tool for classifying the coal pore types, distinguishing movable and unmovable liquid contents, estimating producible and irreducible water porosities, calculating coal reservoir permeability, and evaluating pore size distribution.

4.1. Pore types

The coal pore types have been well studied by many methods including gas adsorption, MIP, and microscopy methods. Pores in coals are composed of two distinct (dual-pore) systems including primary and secondary pores [34]. The primary pore system consists of the micro- and mesopores (<0.1 μm), which contain the majority of the in-place gas volume. The secondary pore system includes macropore (>0.1 μm), microfractures, cleats and natural fractures, forming the conduit for mass (gas and water) transfer to the wellbore. Micro- and mesopores are also called adsorption pores, and macropores are called seepage pores based on a percolation threshold of 0.1 mm [22,23,35].

4.1.1. Pore types identified by $T_2$ distribution

In NMR relaxation, water in smaller pores experiences a greater surface relaxation, and thus relaxes faster than that in larger pores. Therefore, a $T_2$ distribution is similar to a pore size distribution, where each relaxation time corresponds to a pore size: larger pores correspond to longer relaxation time and smaller pores to shorter relaxation time [30].

The $T_2$ distribution characteristics including the number, size and position of $T_2$ spectrum peaks, can be used to analyze coal pore types. As shown in Fig. 1, the distributions of $T_2$ spectra generally have various peaks, which reflect multiple coal pore types. The distributions are commonly bimodal and trimodal, and sometimes unimodal. For the unimodal distribution, a narrow distribution represents a single pore type (Fig. 1i), whereas a wide distribution may represent multiple pore types (Fig. 1k). For multiple peaks, the connection among these peaks can be used to identify the connectivity among pores. For example, the well-connected trimodal distribution in HC3-5 (Fig. 1a) suggests that well-connective multi-pores exist in that coal, while the less well-connected trimodal distribution in WL7 (Fig. 1e) may indicate that three disconnected pore types are present in this coal.
As discussed, all pores and cleats can be measured from a full saturated T₂ spectrum, but only pores <0.1 μm can be measured from an irreducible water-saturated T₂ spectrum. By integrating the two NMR measurements, the adsorption pores (<0.1 μm) and seepage pores (>0.1 μm) can be distinguished. Consequently, in a typical T₂ spectrum (from short to long relaxation times), the adsorption pores, seepage pores and cleats (or fractures) can be identified sequentially. The first T₂ spectrum peak (p1) is associated with adsorption pores that are always well-developed in medium to high rank coals (Fig. 1e–j and l). The second T₂ spectrum peak (p2) is associated with the seepage pores that are found in most samples (Fig. 1a–h, j and k). The p2 is commonly lower than p1 in Groups 1 and 3, which means that the seepage pores are not as well-developed as the adsorption pores in the two groups of coals. The last T₂ spectrum peak (p3) is associated with cleats (or fractures) that are recognized for some samples, such as HC3-5 (Fig. 1a), WL7 (Fig. 1c), STJ1-10 (Fig. 1d), YQ3K-3 (Fig. 1h), XIM12 (Fig. 1j) and G2 (Fig. 1k).

Comparing the NMR measurement in S_w and S_{ir} (Fig. 1e–j and l), it is found that adsorption pores are saturated with irreducible water that cannot be expelled by centrifuging, while cleats are saturated with free water that can be fully expelled by centrifuging. Taking G2 as an example, its T₂ spectrum at S_w shows that the coal contains moderately adsorption pores (p1), and well-developed seepage pores and cleats (p1 + p2). The T₂ spectrum at S_{ir} shows that water in the adsorption pores was not expelled (p1), and water in seepages pores was partially expelled, whereas the water in cleats was completely expelled. In addition, for the T₂ spectrum of G2 at S_{ir}, the p2 and p3 are combined as a new peak (p2 + p3). This means that cleats have very good interconnectivity with seepage pores in the coal. This kind of T₂ spectrum is commonly found in sandstone samples [8]. It can be concluded from these relaxation spectra that the seepage pores, cleats and fractures generally have connective pores and are meaningful for seepage and the mobility of gas and water, while the adsorption pores are generally closed and not favored for the mobility of gas and water.

It should be noted that in some cases, the spectra at S_w and S_{ir} are complex. For example, in coal sample WL7 (Fig. 1c), the spectrum amplitude at S_{ir} is higher than that at S_w for some relaxation time area. The reason for this abnormal case is the poor connectivity of pores in the sample. The poor connectivity causes some water to be retained at the surface or inside adsorption pores after centrifuging, leading to the increase of the relaxation time amplitude [10].

### 4.1.2. Comparing with the results of CT and MIP

NMR-based pore types agree well with the results obtained from porosity, permeability and CT scan of coal samples. As shown in (a) the CT scan image, pores and minerals are represented with dark black and white colors, respectively; (b) the NMR T₂ distribution; and (c) helium porosity and air permeability.
In Fig. 2, five typical coals with various coal ranks demonstrate the relationship among pore types, porosity, permeability and the T2 spectra characteristics. For HC3-5, the well-developed fractures and seepage pores shown in the CT scan image (Fig. 2a) correspond to the T2 spectrum peaks of p2 and p3 (Fig. 2b). This is consistent with the interpretation that well-developed fractures and pores resulted in the high permeability (82.1 mD) and high porosity of the sample (Fig. 2c). For WL7, the p3 peak in the T2 spectrum (Fig. 2b) agrees well with the fractures shown in the CT image (Fig. 2a). Thus, it is reasonable to infer that the moderate porosity and permeability of this sample (Fig. 2c) are mainly contributed by the fractures in the coal. Samples STJ1-10 and SH3 have low porosity and permeability (Fig. 2c). Correspondingly, both of their T2 spectrum peaks are located at <100 ms (Fig. 2b), which means that the cleats and fractures are poorly developed. At the same time, the CT images of both samples (Fig. 2a) show that the pores (in STJ1-10) or cleats (in SH3) are thoroughly filled with minerals [29], which is the main reason for the low porosity and permeability of these two samples. Comparably, G2 has high porosity and permeability (Fig. 2c), well-developed seepage pores and cleats (Fig. 2a), and thus has a large T2 spectrum peak of p2 + p3 (Fig. 2b).

Moreover, the pore types identified by T2 spectra and peaks agree well with the pore structure determined by MIP. Taking YQ3K-3 as an example (Fig. 3), the result by MIP shows that the sample has dominant adsorption pore volumes but a few seepage pore and cleat volumes, which is consistent with the dominant p1 and the small p2 and p3 in the T2 spectra. The seepage pores (Fig. 3) are saturated with producible water that can be expelled by centrifuging. In general, the T2 spectra distribution reflects the pore types and pore size distribution.

4.2. Porosity

In petroleum reservoir characterization, the porosity of sandstones and carbonates is calculated by a model based on the NMR geometric mean T2 (T2g) [7,8,11]. The model uses a statistical relationship between the NMR core measurements and the standard core porosity measurements to estimate porosity. However, this method is very difficult to use for coals because the pore structure of coal is much more complicated than that of sandstones or carbonates. It is also hard to formulate a porosity estimation model by the method used for sandstones due to the lack of sufficient coal samples in this study. Instead, we use the weighted porosity determined by the water saturation method (φw) as an approximation of the NMR porosity (φN), because theoretically these two porosities should be identical. The φw is commonly calculated by estimating a water volume in coal, and the φN is calculated based on the estimation of the signal magnitude of liquid 1H in the water-saturated coal.

Theoretically, the NMR porosity represents the pore volume fractions occupied by bound (irreducible) and free (producible) water. By definition, bound water is the amount of water in coal that cannot be recovered during CBM production, while free water can be recovered. Thus the NMR porosity can be divided into the irreducible porosity (IP) corresponding to the bound water fraction, φw, and the producible porosity (PP) corresponding to free water fraction, φNP. The φNI and φNP can be determined by comparing the T2 spectrum at Sw with that at Sw for the same coal sample.

The φNI and φNP are expressed by

\[ \phi_{NI} = \phi_N \times \frac{BVI}{BVI + FFI} \quad \text{(4)} \]

\[ \phi_{NP} = \phi_N \times \frac{FFI}{BVI + FFI} \quad \text{(5)} \]

where \( \phi_N \), \( \phi_{NI} \), and \( \phi_{NP} \) are the NMR total porosity, IP and PP, respectively; BVI is the bound fluid index (or volume) that can be calculated by the total spectrum area fraction at Sw condition; FFI is the free fluid index (or volume); BVI + FFI represents both the free and bound fluids that can be calculated by the total spectrum area fraction at Sw condition. As shown in Fig. 3, the BVI and FFI are illustrated with the dark-gray color area under the irreducible water spectrum and the light-gray area under the 100% water spectrum. The IP and PP were calculated for seven samples (Table 2). The PP values are low, with a range of 0.07–4.67%, but mostly from 0.1% to 2%. The correlation between PP and total porosity is poor. Some samples with high total porosities may have low PP, and vice versa. The PP values relates to the development of cleats (or fractures) in coals. For example, samples WL7, STJ1–10 and G2 have well-developed cleats (Figs. 1 and 2) and thus have high PP values; whereas YQK15–1A and CZ3 (Fig. 1) are dominated by adsorption pores and thus have very low PP values.
Secondly, the two NMR old that divides the tic relaxation time. Therefore, the bounded water in adsorption pores has characteristics the free water corresponds to seepage pores that can be drained, whereas pores that cannot be easily drained due to capillary forces, while permeability and the pore size distribution.

The estimation of bound and free fluid volumes, as well as the permeability estimated by this model will be discussed below.

4.3. \( T_2 \) cutoff values

By definition, a \( T_2 \) cutoff value \( (T_{2c}) \) is a relaxation time threshold that divides the \( T_2 \) spectrum into two parts: the bound water and the free water. The bound water corresponds to adsorption pores that cannot be easily drained due to capillary forces, while the free water corresponds to seepage pores that can be drained. Therefore, the bounded water in adsorption pores has characteristic relaxation time \( T_2 < T_{2c} \), whereas the free water in seepage pores has \( T_2 > T_{2c} \). The accurate determination of \( T_{2c} \) is a critical step in the estimation of bound and free fluid volumes, as well as the permeability and the pore size distribution.

The process for determining \( T_{2c} \) of coal is the same as that of other rocks [8,11]. An example for the calculation method is illustrated in Fig. 5. Firstly, to calculate \( T_{2c} \), two NMR \( T_2 \) distributions must be obtained: one that corresponds to 100% water-saturated condition \( (S_w) \) and the other to irreducible water condition \( (S_i) \). Secondly, the two NMR \( T_2 \) distributions are transformed into two accumulative \( T_2 \) spectra by the following rule: maximum peak amplitudes (dimensionless) at \( S_w \) and at \( S_i \) are equal to total porosity and IP, respectively (Fig. 5). Finally, two projection processes determine the \( T_{2c} \): the first corresponding to a horizontal projection from the cumulative curve at \( S_w \) and the second corresponding to a vertical projection from the cumulative curve at \( S_i \) (Fig. 5). The \( T_2 \) value at the intersection projected on the \( T_2 \) axis is the \( T_{2c} \).

The calculated \( T_{2c} \) for seven coal samples ranges from 2.5 to 32 ms (Table 2). These values are lower than those from sandstones and carbonates [7,11]. The origin of such differences is uncertain because \( T_{2c} \) is affected not only by lithology, but also by several other factors such as pore-wall chemistry, minor paramagnetic or ferromagnetic components, texture, pore throat to pore body ratios, and other factors not well understood at this time [8,11,12].

4.4. Permeability

Although permeability cannot be directly measured by NMR, it can be estimated based on the porosity and the pore size distribution. For sandstones, two commonly used models have been used to estimate permeability using NMR relaxation data: the free fluid model and the mean \( T_2 \) model. In this section, the two classical models are evaluated and a new model will be discussed.

4.4.1. Free fluid model

The free fluid model (also called Coates model) is based on the Timur–Coates equation [1,8]:

\[
K_c = (\varphi / C) \cdot (\text{FFI} / \text{BVI})^2
\]

where \( \varphi \) is the NMR porosity, \( C \) is a constant, and \( K_c \) is the permeability estimated by this equation. The FFI/BVI is determined by the \( T_{2c} \) that divides the \( T_2 \) distribution into the bound water part (BVI) and free water part (FFI), as shown in Figs. 3 and 5. In well logging applications, a fixed \( T_{2c} \) is commonly used. For example, sandstone and carbonate are commonly assigned a \( T_{2c} \) value of 33 and 92 ms, respectively [7,11]. The empirically derived constant \( C \) is

---

**Table 2**

Porosity from NMR measurements, \( T_2 \) cutoff, and permeability by Coates- and PP models.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \varphi_0^a ) (%)</th>
<th>( \varphi_i^a ) (%)</th>
<th>FFI/BVI</th>
<th>( T_{2c}^b ) (ms)</th>
<th>( K_c^d ) (mD)</th>
<th>( K_p^d ) (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W17</td>
<td>0.45</td>
<td>2.76</td>
<td>6.13</td>
<td>31</td>
<td>3.32</td>
<td>3.25</td>
</tr>
<tr>
<td>ST11-10</td>
<td>0.36</td>
<td>0.49</td>
<td>1.36</td>
<td>11</td>
<td>0.00088</td>
<td>0.16</td>
</tr>
<tr>
<td>YQ2K15-1A</td>
<td>3.63</td>
<td>0.34</td>
<td>0.09</td>
<td>32</td>
<td>0.002</td>
<td>0.09</td>
</tr>
<tr>
<td>YQ3K-3</td>
<td>1.03</td>
<td>0.71</td>
<td>0.69</td>
<td>24</td>
<td>0.0036</td>
<td>0.29</td>
</tr>
<tr>
<td>XM12</td>
<td>3.92</td>
<td>1.17</td>
<td>0.3</td>
<td>30</td>
<td>0.049</td>
<td>0.63</td>
</tr>
<tr>
<td>G2</td>
<td>1.21</td>
<td>4.67</td>
<td>3.86</td>
<td>12.5</td>
<td>14.69</td>
<td>15.04</td>
</tr>
<tr>
<td>CZ3</td>
<td>0.96</td>
<td>0.07</td>
<td>0.07</td>
<td>2.5</td>
<td>0.00049</td>
<td>–</td>
</tr>
</tbody>
</table>

---

**Fig. 4.** Exponential relationship between the air permeability and the producible porosity.

**Fig. 5.** NMR measurements at 100% water-saturated condition \( (S_w) \) and irreducible water condition \( (S_i) \) of sample G2 show the method to calculate a \( T_2 \) cutoff value \( (T_{2c}) \).
related to the characteristic rock or formation. For sandstones, an experiential value of \( C = 6.2 \) is commonly given [8].

In order to quantify the Coates model for coal, the constant \( C \) needs to be determined first. According to Eq. (6), \( C \) is the linear slope of the correlation between \( \phi_2/2K_s \) and \( \sqrt{K_s} \), the measured air permeability. Based on linear regression analyses, a goodness-of-fit of 0.99 and \( C = 5.9 \) are obtained. As a result, the Coates model for coal is defined as

\[
K_c = \left( \phi/5.9 \right) \times \left( \text{FFI}/\text{BVI} \right)^2
\]  

(7)

Based on Eq. (7), the \( K_c \) values for seven coal samples were estimated and listed in Table 2. Although the estimated \( K_c \) shows a strongly positive correlation with the measured \( K_s \), the error is still large. Especially for samples STJ1-10, YQ2k15-1A and XIM12, the estimated values generally are one order of magnitude smaller than the actual values.

4.4.2. Mean \( T_2 \) model

The mean \( T_2 \) model (also called SDR model) can be formulated in several ways [8,11], among which Eq. (8) is a commonly used expression:

\[
K_s = C_1 \phi^4 \times T_2 g^2
\]  

(8)

where \( T_2 g \) is the geometric mean of the \( T_2 \) distribution at saturated water condition; \( \phi \) represents the NMR porosity; \( C_1 \) is a constant related to the characteristic rock or formation, and \( K_s \) is the NMR permeability estimated by this equation.

To estimate the value of \( C_1 \), the \( \phi^4 T_2 g^2 \) is plotted against \( K_s \). If Eq. (8) is valid for coal, then \( \phi^4 T_2 g^2 \) and \( K_s \) should be linearly correlated, and the slope of the straight line should be \( C_1 \). Unfortunately, our results show that the measured data cannot be correlated, which means that the SDR model does not work for coals.

The SDR model is not suitable for coal for several reasons. The principal reason is that the porosity considered in the SDR model is the total porosity and not the PP, although the latter is much more important for coal permeability. Another reason relates to the complicated pore structures among these samples with various coal ranks. The third reason may be that degassing and vacuuming prior to the NMR experiment did not adequately discharge some hydrocarbons such as methane. Hydrocarbons can change the air condition; \( \phi \) represents the NMR porosity; \( C_1 \) is a constant related to the characteristic rock or formation, and \( K_s \) is the NMR permeability estimated by this equation. To estimate the value of \( C_1 \), the \( \phi^4 T_2 g^2 \) is plotted against \( K_s \). If Eq. (8) is valid for coal, then \( \phi^4 T_2 g^2 \) and \( K_s \) should be linearly correlated, and the slope of the straight line should be \( C_1 \). Unfortunately, our results show that the measured data cannot be correlated, which means that the SDR model does not work for coals.

4.4.3. PP model

As discussed earlier, two classic models express permeability as a function of porosity. The difference between them is that the Coates model relates to the parameter of the free fluid fraction in coal, while the SDR model relates to the parameter of the geometric mean of relaxation time distribution.

Since most pores in coal refer to closed pores that do not contribute to permeability, the parameter of PP may be much better than the total porosity for permeability estimation. As shown in Fig. 4, the air permeability strongly correlates with the PP. Indeed, an exponential regression between air permeability and PP shows a great goodness-of-fit (\( R^2 = 0.997 \), Fig. 4). Based on the regression result in Fig. 4, the PP model can be defined as:

\[
K_p = 0.49 \exp(\phi_p/135) - 0.54
\]  

(9)

where \( \phi_p \) is the PP by NMR analysis, and \( K_p \) is the estimated NMR permeability.

The estimated NMR permeability by the PP model is listed in Table 2. When comparing \( K_p \) with \( K_s \), it is found that, except the values for YQ3K-3 (with a high error) and CZ3 (with an unreasonable value <0), the difference between the estimated values and the actual values is within an order of magnitude. The PP model is valid for permeability estimation, especially for highly permeable samples. Moreover, the PP model may be improved by adding more sample data, dividing them into their specific coal ranks and applying different coefficient or constant in Eq. (9) for each type of coal.

4.4.4. Comparison of the three models

Except for the SDR model, both Coates and PP models can be used to evaluate the relative size of permeability among coal samples. By comparison, the PP model provides much better estimation than the Coates model because the permeability of coal is more relevant to the PP than to the total porosity (integration of PP and IP). Moreover, the PP model requires only the parameter of PP, thus it is more convenient to use than the other models.

It needs to be noted that both the Coates model and the PP model do not work well for low permeable coal. For both models, the magnitude of estimation error is large when the actual permeability is lower than 0.1 mD. This phenomenon may be due to the following three reasons. Firstly, the number of samples is limited and at the same time, differences between these samples are huge. These NMR permeability models were developed using coal samples from the sub-bituminous to anthracite, thus the petrophysical differences (e.g. pore structure and permeability) are large for these samples (Tables 1 and 2). The biggest problem faced by all of the models is the fact that the air permeability spans over a large range of values (0.00032–14.9 mD), while the NMR parameters used in the models do not change significantly. Therefore, it is difficult for any model to estimate the permeability with a million-fold span value. Secondly, a weakness of these models is that they assume a strong and constant relationship between porosity and permeability, which is a result of similar pore body and pore throat distributions, as is the case for sandstones. However, for coal, pore types and structures (including micro-, meso- and macropores, and cleats) may in fact be very different due to many changes that occur during coalification [34–36]. For the studied samples, the correlation between porosity and permeability may be much weaker, and eventually, induces large differences between the NMR permeability and the air permeability. Finally, the error in the estimated permeability may relate to the differences in the measurement methods themselves. The air permeability is measured by air, while the NMR permeability estimation is based on the measurement of water in coal. The problem may exist for scaling the NMR permeability by air permeability.

4.5. Pore structure based on NMR relaxation

Although NMR relaxation and MIP are different in theory, they show high coincidence in studying pore types and pore structures. As seen in Fig. 3, when a shift is applied to the \( T_2 \) distribution, it shows a remarkable correlation with the pore size distribution by MIP. This kind of similarity is seen in all selected samples and suggests that a characteristic relationship may exist between the pore structure by NMR and that by MIP. If this is the case, the pore structure study by MIP may be substituted by the study by NMR, and on the other hand, MIP could verify pore structure results concluded by NMR. For this purpose, accurately scaling the NMR pore structure result by MIP data will be further discussed.

According to Eq. (3), when a constant \( F_i \) is given [6], the equation can be transformed into

\[
1/T_2 = F_s + \rho_g/r_c
\]  

(10)

where \( F_s \) is the pore geometry morphologic factor, with \( F_s = 3 \) for spherical pores; and \( r_c \) is the estimated pore size corresponding to a \( T_2 \) value. Given a constant \( C_1 \), Eq. (10) can be transformed into
Based on Eq. (11), numerous researchers have proposed many transform methods to obtain the pore structure or capillary pressure curves from NMR data [37]. These methods are proven suitable or partly suitable for sandstone, but not for the coals used in this study. This is because these methods are not convenient and difficult to apply to coal and they have large estimation error especially for the coals with multiple peaks in this $T_2$ spectrum. Here a new method for scaling the NMR pore structure is proposed.

The method is based on the principle that any relaxation time in the $T_2$ distribution corresponds to a certain pore size of the coal sample; slow relaxation times correspond to large pores and versa. To quantify the relationship between relaxation time and pore size, a key parameter of $T_2c$ is used. Since $T_2c$ was determined by a centrifuge experiment and two NMR experiments, the pore size ($r$) corresponding to the certain $T_2c$ can be determined. For any relaxation time ($T_2$) in a $T_2$ relaxation distribution, the corresponding pore size ($r_{ci}$) can be determined by Eq. (12).

$$r_{ci} = r + T_2c/T_2$$

(12)

where $r$ ($\mu$m) is the pore size corresponding to the $T_2c$; and $r_{ci}$ ($\mu$m) is a pore size corresponding to a relaxation time $T_2$ (ms). For any sample, $r$ is a constant and corresponds to the minimum pore size that the centrifuge experiment can reveal. As discussed in Section 3.2.3, $r$ is about 0.1 $\mu$m in this study. Based on Eq. (12) and $r = 0.1 \mu$m, the pore size distribution by NMR data is determined.

The pore size distribution is scaled for seven coals, among which four representative samples are shown in Fig. 6. The result shows that the constructive pore size distributions coincide very well with the pore size estimated from MIP, and therefore the pore structure estimated by NMR is reliable.

Further comparison of the two pore structures indicates that the pore structure estimation on adsorption pores (<0.1 $\mu$m) is more accurate than that on seepage pores (>0.1 $\mu$m) (Fig. 6). The error in estimating the seepage pores may be explained as follows. MIP is a common method for characterizing porous structures, but it has a drawback in coal characterization because of the compressibility of coal [24]. The MIP is based on the Washburn equation: increasing pressure makes smaller pores accessible to mercury. At the early intrusion phase with lower mercury pressure, mercury abruptly intrudes into the pores and intrusion volume increases rapidly. At this stage, the pressure and the intrusion volume do not match well with the Washburn equation. This phenomenon commonly results in overestimations of intrusion volume and the proportion of macropores. Comparably, as a nondestructive method, NMR does not overestimate the macropore proportion. This is why the two pore structures show a greater difference in their large pore fraction. The other reason may be the differences inherent to the measurement principle between NMR and MIP. NMR responds to the pore body size whereas MIP is controlled by the pore throat size (the narrowest pathway connecting two pores in the network). For some coals with high pore heterogeneity, the differences between pore body and pore throat are significant, thus the pore structure estimated by NMR for these coals would be very weak.

In general, the NMR relaxation has shown potential advantages for the petrophysical characterization of coal in several ways. Firstly, it is a nondestructive technique. NMR does not require special shape or size in sample preparation, and the method does not generally destroy the original pore structure of coal. Secondly, it is the only method that fits well for in situ CBM reservoir. The in situ CBM reservoir is commonly saturated with water that is similar to the measurement condition of NMR. Thirdly, it is an instant detection method and can be easily applied to drill cores in well field. Lastly, with further research it may provide a very promising technique for well logging.

5. Conclusions

This study has shown that pore types of coal can be classified by measuring NMR $T_2$ distributions. NMR $T_2$ distributions for 100% water-saturated samples are commonly bimodal, unimodal and multimodal, with peaks of adsorption pores (<0.1 $\mu$m) at 0.5–2.5 ms, seepage pores (>0.1 $\mu$m) at 20–50 ms, and the cleats (or fractures) at >100 ms.

The IP and PP values are estimated using NMR data of cores at 100% water-saturated and irreducible water conditions. The PP value of coals is low, in the range of 0.07–4.67%, but more commonly

$$R_e = C_2 * T_{2c}$$

(11)
between 0.1% and 2%. PP strongly relates to the developments of cleats (or fractures) and the air permeability of coals.

Based on an exponential regression of air permeability and PP, a new NMR-based permeability model is proposed. This model provides significantly better permeability estimations than the classic (Coates and SDR) models originally developed for sandstones. In combination with mercury intrusion porosimetry, we also propose a NMR-based pore structure model that efficiently estimates the pore size distribution of coals.

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