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Research on Tectonic Coal Structure Based on NMR Technology

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ABSTRACT
The understanding of coal body structure has important research significance for the prevention of coal and gas outburst and the development of coalbed methane. In order to further determine the difference between the primary structure coal and the structural microstructure of coal mines, and analyze the coal bed gas storage and migration control mechanism of coal body structural characteristics, the microstructure of structural coal in Sihe Coal Mine was tested by NMR technology. The structural characteristics of the coal body were mainly analyzed by obtaining maps, and the structural information of C, H, O and other related functional groups was quantitatively analyzed. The research results provide a technical reference for the study of coal microstructure.
Keywords: *Tectonic coal structure, NMR technology, micro structure, functional groups.*

1. INTRODUCTION

Tectonic coal is formed from primary structural coal that undergoes different degrees of fragmentation, toughness, plastic deformation, and rheological migration under the action of structural stress. They are different, and also have certain structural deformation characteristics in terms of microcrystalline structure, macromolecular structure arrangement, and pore and fissure morphology. This deformation feature results in low strength of tectonic coal, which is the easiest to be destroyed and thrown out, and the occurrence and movement control of coal seam gas is more complicated [1-2]. In recent years, scholars at home and abroad have proposed the use of infrared spectrometers, nuclear magnetic resonance instruments, X-ray diffractometers, and scanning electron microscopes to measure and analyze coal structures, and to obtain information about coal structures [3-6]. Therefore, this paper uses nuclear magnetic resonance (NMR) method to quantitatively analyze the main functional groups of tectonic coal, and to study the microstructural differences of tectonic coal. It provides a theoretical basis and technical guidance accident prevention and effective exploitation of coalbed methane resources.

2. EXPERIMENTAL PRINCIPLE

Nuclear magnetic resonance (NMR) is generated by the motion of nuclear spins[7]. When an atomic nucleus with an odd number of nucleus spins, it can generate a magnetic field or a nuclear moment, such as: 1H (hydrogen), 13C (carbon). The NMR information of the detected object can be obtained according to this phenomenon, and the Fourier transform and reconstruction imaging can be performed by the computer according to the difference in relaxation time. When the nuclear system of the detected object in the static magnetic field receives the electromagnetic wave of the corresponding frequency, a resonance transition occurs between its magnetic energy levels. The entire process of nuclear magnetic resonance takes place in a huge external magnet cavity, which can generate a constant and strong static magnetic field (B0) (as shown in Figure 1), superimposing another small RF magnetic field on the static magnetic field, nuclear excitation and induction of nuclear magnetic resonance (B1), and then superimposed a small gradient magnetic field for spatial tracing and control of spectral imaging. In addition, the absorption and release of energy between nuclei will also cause resonance. The energy would be absorbed by hydrogen protons at low energy levels is exactly equal to the energy level difference, and it will transition to a high energy level. If the energy released by hydrogen protons is exactly equal to the energy level difference, and It can fall back to a low energy level. This kind of fluctuation of the nucleus is performed in the same magnetic field, the state of the hydrogen atomic nucleus before and after entering the magnet changes.

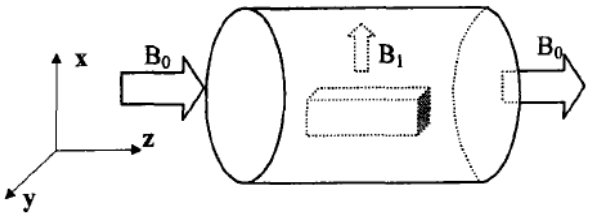

Figure 1 Magetostatic field B_0 and RF magnetic field B_1

The nuclear magnetic resonance experiment is essentially based on the differences in the components and structural characteristics of the test object. The relaxation process uses the resonance phenomenon caused by the interaction of the atom with nuclear magnetism and the external magnetic field according to the change of the observed signal intensity to carry out experiments and detection. Therefore, NMR technology can detect both the macromolecular structure characteristics of porous media and some physical properties: flow parameters, interactions between porous media frameworks. NMR technology can directly obtain maps and analyze the structural characteristics of non-destructive samples during imaging. It can provide quantitative or semi-quantitative structural information of related functional groups such as C, H, O. At present, this technology is analyzing and studying fossil energy (coal, kerogen). Etc.) have been widely used in this process. This time, NMR tests were used to study the four types of coal with different coal body structures collected under the Sihe mine.

3. NMR PARAMETER CALCULATION

Agate grinding was performed on the four types of coal samples collected (primary structural coal, cracked coal, crushed coal, and mylonite coal). Sample testing was completed at the Beijing Institute of Petrochemical Technology, Chinese Academy of Sciences, and the instrument used was an Advance III400 nuclear magnetic resonance spectrometer produced by Veeco. During the experiment, ^{13}C NMR techniques such as cross polarization (CP), magic angle rotation (MAS), and sideband suppression (TOSS) were used to study the coal structure and its evolution characteristics. The RF field strength of ^{13}C in the experiment is 64 kHz, the frequency of high-power decoupling protons is 400.119 MHz, the rotor operating speed is 4 kHz, the cross-polarization contact time is 1.0 ms, the repetitive delay time is 2s, the data collection is 1024, and the number of accumulations is 500 times. The four 180 ° pulsed rotating sideband suppression techniques of the TOSS echo program of Dixon (1982) are used to make the rotating sidebands of aromatic carbon atoms converge on isotropic peaks. The entire sample spectral width is 50 kHz. Due to the complexity of the chemical structure of coal macromolecules and the characteristics of coal solid nuclear magnetic resonance technology, the ^{13}C-NMR spectrum of coal samples will be limited in its ability to resolve, and there are only two peak groups in the range of 0 ~ 220 μg/g of the conventional spectrum. In order to further study the chemical structure characteristics of tectonic coal, the NMR test samples of the Sihe mine are all simulated peak-splitting procedures, and the spectral peak fitting and peak de-stacking are performed. The result of peak fitting for coal ^{13}C NMR spectrum are as shown in Figure 2.

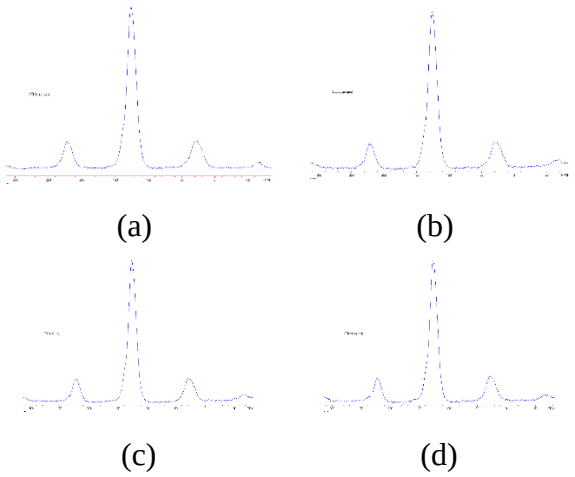

Figure 2 Result of peak fitting for coal ^{13}C NMR spectrum

From the Figure 2, 6~10 small peaks were separated for each sample spectrum. In order to obtain more relevant information about the structure and chemical composition of coal, computers have been widely used at home and abroad to fit the spectrum and unfold the peaks, as shown in Table 1.

Table 1 Chemical distance attribution of coal ^{13}C NMR spectrum

Chemical shift/ppm	Main attribution	Chemical shift/ppm	Main attribution
14–16	Terminal methyl group	100–129	Proton aromatic carbon
16–22	Methyl on ring	129–137	Bridging aromatic carbon
22–36	Methylene, methine	137–148	Alkyl substituted carbon
36–50	Quaternary carbon, a-position carbon on aromatic ring	148–164	Aryl-substituted aromatic carbon
50–56	Methoxy	164–188	Carboxyl carbon
56–75	Lipid carbon attached to oxygen	188–220	Carbonyl carbon
75–90	Carbon attached to oxygen in carbohydrate rings		

4. ANALYSIS OF EXPERIMENTAL RESULTS

Based on the above-mentioned nuclear magnetic resonance spectroscopy (NMR) parameter calculation method, the ^{13}C NMR (CP / MAS + TOSS) spectra of the four types of coal samples in Sihe Mine were subjected to

peak separation simulation and data processing to obtain the relative percentage content of each carbon functional group in the four types of coal body structure coal samples (as shown in Table 2). Because the peaks corresponding to the proton-containing aromatic carbon and bridged aromatic carbon overlap more severely, they cannot be separated by a peak-separation simulation program so that it is counted as an index and recorded as $fa^{H,B}$. Similarly, the arylmethyl carbon and the aliphatic methyl carbon cannot be separated from each other, which is also regarded as an indicator, which is recorded as $fal^{a,3}$. The quaternary carbon, methine carbon, and methylene carbon cannot be divided into peaks, and it is recorded as $fal^{*,1,2}$. The evolution characteristics of the NMR structural parameters of each functional group will be explained separately by the peak division simulation.

Table 2 Results of NMR parameters of experimental tectonized coals (%)

No.	I	II	III	IV
f_a	63.47	64.56	62.87	65.31
$f_a^{H,B}$	56.89	57.28	57.97	58.34
f_a^S	4.64	5.60	3.69	5.99
f_a^O	1.94	1.68	1.21	0.98
f_a^{COOR}	2.89	4.22	1.46	3.57
$f_a^{C=O}$	0.61	0.32	0.43	0.88
f_{al}	27.69	27.13	26.71	25.12
$f_{al}^{a'\ 3}$	8.74	7.13	6.97	6.25
$f_{al}^{*,1,2}$	17.15	16.88	18.16	16.13

In the Table 2, f_a: aromatic carbon ratio; $f_a^{H,B}$: proton-containing aromatic carbon and bridged aromatic carbon; f_a^S: alkyl substituted aromatic carbon;f_a^O: oxygen-linked aromatic carbon; f_a^{COOR}: carboxyl carbon; $f_a^{C=O}$: carbonyl carbon; f_{al}: fat carbon ratio; $f_{al}^{a'\ 3}$: aryl methyl and aliphatic methyl carbon; $f_{al}^{*,1,2}$: Quaternary carbon, methine carbon and methylene carbon; f_{al}^O: Oxygen-bonded carbon.

(1) $f_a^{H,B}$ is the main components of aromatic carbon in the chemical structure of coal, which can be used to reflect the aromatization of coal and the increase of aromatic fused rings. From the analysis of the map, it is shown that with the increase of the degree of destruction of the coal body structure, the proportion of proton-containing aromatic carbons and bridging aromatic carbons has increased, indicating that tectonic evolution can significantly promote the process of coal aromatization and aromatic condensing. The change law of f_a^S is not obvious, but it is less than 6% overall, which indicates that the high metamorphic anthracite promotes the substitution of alkyl on the aromatic ring during the long-term metamorphic evolution and promotes the alkyl to fall off.

The overall change trend of f_a^O oxygenated aromatic carbon has a negative correlation with the increase in the degree of coal destruction. The change law of carboxyl carbon and carbonyl carbon is not obvious, but the overall content is low, indicating that the reflectance of the vitreous group is higher in the stage of highly metamorphic anthracite. The content of oxygen-containing aromatic carbon, carboxyl carbon and carbonyl carbon itself is already very small, and less oxygen functional group shedding occurs.

(2) The aliphatic carbon corresponding to the aromatic carbon is one of the important macromolecular structure components in coal, and its evolution law is opposite to that of aromatic, and it decreases as the maximum reflectance ($R_{o,max}$) of the vitreous group increases.

$f_{al}^{a'\ 3}$ is not significantly affected by the reflectance of the vitrinite group, but it is more obviously controlled by the structure. $f_{al}^{*,1,2}$ *has* no significant change in the reflectivity with the vitrinite group.

However, it generally shows that with the strengthening of the deformation and deformation of the structure, the unpaired electrons formed in the early stage gradually begin to recombine into bonds, and the alkyl group may fall off into hydrocarbons in the process, which will make the $f_{al}^{a'\ 3}$ decrease greatly. However, $f_{al}^{*,1,2}$ will increase to different degrees. The decrease or increase in their magnitude indicates that the strong tectonic strain environment can promote the recombination of broken bonds. The change pattern of f_{al}^O is not obvious.

5. CONCLUSION

The NMR structural spectrum of the structural coal in the Sihe Mine shows the characteristics of both the structural deformation and the reflectance of the vitrinite group. However, for different functional group structure parameters, there is a certain difference in the degree of influence of structural deformation and vitrinite reflectance. Through the study of the microscopic differences of the coal body structure, it is beneficial to deepen the study of the structural coal structural characteristics and the control mechanism of the occurrence and migration of coalbed methane.

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