STUDY OF FOSSIL COALS IN THE KUZNETSK BASIN BY EPR SPECTROSCOPY

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Abstract. Fossil coals of the Kuznetsk Basin of varying degrees of metamorphism were studied by the method of electron paramagnetic resonance. It is shown that in the series from brown coal to anthracite, the g-factor of the EPR signal decreases, due to the aromatization of the carbon framework and a decrease in oxygen-containing and hydrogen-containing fragments in the coals. The maximum width of the EPR spectrum is observed for coals of the middle stage of metamorphism, which indicates the presence of both aliphatic and aromatic paramagnetic centers (PCs) in their structure. Also, in the series of coal metamorphism, the concentration of PCs increases. Thus, it has been shown that in the process of coal metamorphism, a change in the electronic structure occurs, associated with the rearrangement of the carbon skeleton of the organic mass of coal (OMC) and a decrease in the amount of oxygen-containing and hydrogen-containing radicals.

1. Introduction
Coals have paramagnetism, which is associated with the content of two different types of paramagnetic centers, caused by stabilized aromatic free radicals and conjugated aromatic systems, whose signals overlap [1]. In this case, for coals with low degrees of metamorphism, paramagnetic centers in the hydrocarbon structure, unpaired electrons in the carbon matrix for anthracites, and both types of centers for coals of medium metamorphism, the superposition of which determines the value of the g-factor, are decisive.

In the metamorphism of coals, a fundamental tendency to simplify the multicomponent structure is manifested, accompanied by a number of physicochemical transformations, in which the stages of quantitative changes alternate with qualitative transformations of the chemical composition and restructuring of the hydrocarbon substance. Each qualitatively new state of the coal substance will differ in paramagnetic properties, and, consequently, in the value of the g-factor [2]. Significant for the process of metamorphism of fossil coals is the transition from a relatively homogeneous CH-structure with an insignificant fraction of the centers of the C-phase (in size and concentration) through the stage of maximum heterogeneity (with a comparable concentration of CH- and C-phases) to a quasi-homogeneous C-phase with individual inclusions CH-phase (high degree of metamorphism) [2-3]. It is noted that the g-factor of the EPR signal of coals decreases with an increase in the stage of metamorphism, which is associated with a decrease in the amount of oxygen-containing and hydrogen-containing radicals [4].
2. Objects and technique

The following coals of the Kuznetsk Basin were used as the object of research: grade B, mine Kaichak; brand LF, mine "Kamyshansky" Severo-Taldinskoye deposit, seam 73; LFG grade, V.D. Yalevsky mine, seam number 52; brand G, Kirov mine, Polenovsky seam; grade F, Tikhov mine, seam No. 23; grade C, LLC “Area Koksovy”, seam II internal; grade SLC, mine "Tomusinsky"; WC grade, mine "Bachatsky"; grade L, JSC Kuznetskinveststroy, seam 19a; grade A, mine "Bungurskiy". Technical analysis, as well as the elemental composition of the organic mass of coal (OMC) are presented in Table 1.

Table 1. Results of technical analysis and elemental composition of coals.

| Coal* grade | Technical analysis, % | Elemental analysis of OMC, % |
|-------------|-----------------------|------------------------------|
|             | $W^a$     | $A^d$     | $V_{daf}$ | C  | H  | N  | S  | O  |
| B           | 11.8      | 10.1      | 53.1      | 61.4 | 5.1 | 1.0 | 0.5 | 31.9 |
| LF          | 7.6       | 6.2       | 44.5      | 74.4 | 5.3 | 2.3 | 0.5 | 17.5 |
| LFG         | 5.7       | 4.7       | 42.6      | 74.3 | 5.3 | 2.3 | 0.3 | 17.7 |
| G           | 1.2       | 3.3       | 40.4      | 81.3 | 5.8 | 3.1 | 0.2 | 9.6  |
| F           | 0.8       | 7.8       | 33.3      | 80.2 | 5.2 | 3.0 | 0.4 | 11.2 |
| C           | 0.6       | 4.9       | 21.3      | 87.7 | 4.6 | 2.2 | 0.4 | 5.1  |
| SLC         | 0.1       | 6.7       | 19.8      | 84.8 | 4.2 | 2.0 | 0.3 | 8.7  |
| WC          | 1.3       | 4.7       | 19.0      | 83.8 | 4.0 | 2.1 | 0.1 | 10.0 |
| L           | 0.5       | 6.2       | 14.4      | 89.7 | 4.1 | 2.0 | 0.4 | 3.8  |
| A           | 0.4       | 3.6       | 7.7       | 89.6 | 3.3 | 1.8 | 0.4 | 4.9  |

Note. *coal grades: B – brown, LF long-flame, LFG long-flame gas, G – gas, F – fat, C – coking, SLC – semi-lean caking, WC – weakly caking, L –lean, A – anthracite; $W^a$ – analytical moisture; $A^d$ – ash content; $V_{daf}$ – yield of volatile substances.

EPR spectra were recorded on a Bruker EMX 6/1 micro spectrometer in the X-band (9.5 GHz), with the instrument settings: magnetic field sweep range $\Delta H = 1300-5600$ G; signal amplification factor $2.24 \cdot 10^2$; attenuation of microwave power 20 dB; signal conversion time 15 ms; signal sweep time 31 s.

The samples under study were weighed ($m = 15 \pm 0.5$ mg) and placed in ampoules made of ultrapure quartz, which did not give EPR signals. The ampoule with the sample was placed in the resonator of the spectrometer, after which the EPR spectra were recorded. All samples were tested under identical conditions.

3. Experimental results

EPR spectra of the studied coal samples have a similar character. As an example, Figure 1 shows the EPR spectrum of a sample of LF coal.
Figure 1. EPR spectrum of a sample of LF coal. The sweep width of the magnetic field is 4400 G. Inset - EPR spectrum of LF coal sample. The sweep width of the magnetic field is 150 G, the power attenuation is 20 dB.

In the EPR spectra of all studied coal samples, there are no extraneous signals, or they are comparable to the noise level. An exception is the EPR spectrum for a sample of grade B coal. At 1600 G, an additional signal is present in the spectrum of grade B coal, which is produced by Fe^{III}.

The signal of the first derivative of the absorption of the samples is asymmetric (inset in Fig. 1), which indicates the presence of at least two different types of paramagnetic centers with different g-factors [5].

The absorption line width can be determined from the spectra. It is known [6] that a broad line is observed when the structure contains a significant number of aliphatic structures. It is also noted that in coals a broad signal is associated with spin exchange in the presence of paramagnetic metal and oxygen ions, the mechanism of action of which is to reverse the direction of the spin magnetic moment of an electron when interacting with an unpaired electron [7]. For the studied coal samples, the widths of all spectra, without division into signal components, do not exceed 6 G. The maximum width of the spectrum was recorded for samples of coals of grade F and grade G (6.74 G), the minimum - for coal of grade WC - 4.45 G. Narrow bands are associated with the formation of condensed polycyclic aromatic compounds [8].

To determine the concentration of PC in the studied coal samples, EPR spectra were recorded in the presence of Mn^{2+} as a standard. As an example, the spectrum of a LF coal sample is shown (Fig. 2).
The characteristics of the EPR spectra of coals of various degrees of metamorphism are shown in Table 2.

**Table 2.** The characteristics of the EPR spectra of coals of various degrees of metamorphism

| Coal grade | PCs/g, av. | g-factor | ΔH, G | I, rel. units |
|------------|------------|----------|-------|--------------|
| B          | 3.0747E+18 | 2.00388  | 5.97  | 0.16E+6      |
| LF         | 2.1019E+19 | 2.00356  | 5.59  | 0.96E+6      |
| LFG        | 1.8123E+19 | 2.0035   | 5.59  | 0.95E+6      |
| G          | 1.9382E+19 | 2.00348  | 6.74  | 0.71E+6      |
| F          | 4.2821E+19 | 2.00339  | 6.74  | 1.75E+6      |
| C          | 6.8231E+19 | 2.00326  | 4.58  | 2.8E+6       |
| SLC        | 8.9651E+19 | 2.00326  | 5.21  | 3.0E+6       |
| WC         | 9.3964E+19 | 2.00327  | 4.45  | 4.6E+6       |
| L          | 8.0807E+19 | 2.00325  | 4.70  | 4.4E+6       |
| A          | 8.7589E+19 | 2.00326  | 4.83  | 6.0E+6       |

It is known that with an increase in the degree of metamorphism in coals, a decrease in the content of volatiles and an increase in the content of carbon are observed. To illustrate the relationship between the paramagnetic properties of coals and their maturity, Figures 3 and 4 show the dependences of the g-factor on the content of volatiles and carbon.
Figures 3 and 4 show that there is a regular change in the g-factor associated with structural transformations in coal, where it transforms into a more condensed state with a decrease in the number of aliphatic structures.

The signal intensity of the EPR spectra of coals depends on the number of paramagnetic centers. Figures 5 and 6 show the dependence of the PC concentration on the content of volatiles and carbon.

Figures 5 and 6 show that the concentration of paramagnetic centers increases with an increase in the degree of metamorphism.

4. Conclusion

It was shown by EPR spectroscopy that in the process of coal metamorphism, a change in the electronic structure occurs, associated with the rearrangement of the carbon skeleton of the OMC and a decrease in the amount of oxygen-containing and hydrogen-containing radicals.

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References
[1] B. I. Losev et al 1959 Dokl. USSR Academy of Sciences 125 (4) 814–816
[2] Adashkevich S. et. al 2000 Polish Journal of Applied Chemistry 44(2-3)139–144
[3] Kucherenko V. A. et al. 1983 Solid Fuel Chemistry 1 9–12
[4] Rusyanova N. D. 2003 Uglekhimiya (Moscow: Nauka) p. 316
[5] Munkhtsetseg S et al 2007 Bulletin of BSU 1 (3) 49–55
[6] Pilawa В. et al 1995 Fuel 74(11) 1654-57.
[7] Lishtvan I. I. et al. 1999 Solid Fuel Chemistry 4 50
[8] Ajit R. et. al 1999 Journal of Catalysis 1(84) 29–38