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The Impact of Microwaves of Different Timing on the Structural and Chemical Characteristics of a Carbonaceous Natural Material

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Abstract. Changes in the properties of brown Kansk-Achinsk coal after exposure to microwaves have been studied using scanning electron microscopy (SEM) and electron magnetic resonance (EMR). The size composition of the samples has been investigated. The structure of coal has been found to be similar to the structure of multicomponent organic glass. The analysis of the changes in the EMR spectra of the coal samples (300 K, 83 K) exposed to microwaves has been found to gather information about the structural transformation taking place in the coal matter.

Introduction

Coal is a natural polymer [1, 2]. The main bulk of the organic part of coal (OPC) is a complex mixture of organic compounds comprising aliphatic and aromatic structures arranged as a three-dimensional polymer of an irregular structure; the rigidity of its framework is determined by the internal donor-acceptor bonds (Fig. 1a). The supramolecular structure of the organic part of coal includes amorphous and crystalline chaotically arranged graphite-like areas (Fig. 1b).

The existence of a phase with graphite-type atomic packing in the coal was experimentally proved [3].

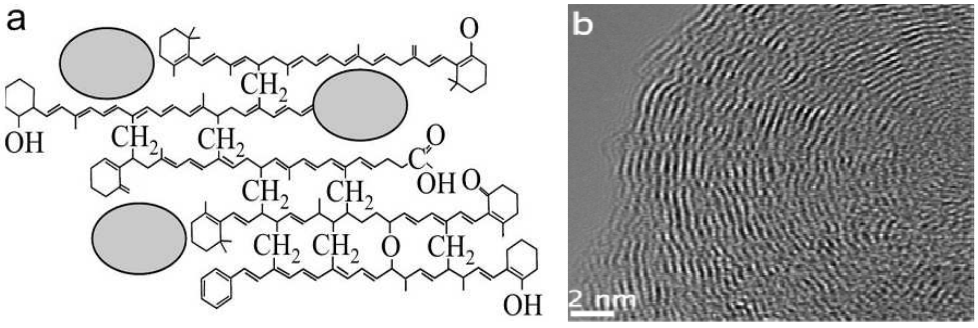

Fig. 1. (a) Coal structure of coals; ovals are graphite-like structures [1]; (b) ordered graphite-like structure in the coal [3]

The current development of microwave treatment of coal is aimed at improving its quality. Microwave impact decreases the moisture content and ash content of coal, and it improves its dispersion [4]. Microwave radiation dielectrically heats coal through the changes in the molecules' orientation in space under the effect of external electric field. The heating disrupts intermolecular bonds.

Benefits of microwave heating:

- concentration of high power energies in small volumes;
- penetration of radiation into the whole volume of processed material;
- high efficiency ($\eta > 90$ %).

The coal matter is diamagnetic. OPC comprises various oxygen-containing functional groups with dipole moment (polar groups). Their number decreases in the series from brown coals to anthracites [5, 6]. Brown coals feature developed porous structure, and are specified by elevated moisture content. Water exists in different forms (from free to bound or crystalhydrate). Water has a profound impact on pyrolysis, gasification, liquefaction and combustion of coal.

In this work, brown Kansk-Achinsk coals were dehydrated by microwave technology, which according to [9] is the most efficient to process materials with high number of polar molecules (wood, peat, brown coal).

Experimental Technique

The coal under study was brown Kansk-Achinsk coal (ash content 8%, moisture content 20%) after microwave drying for 60 and 120 seconds in an 850-watt microwave oven.

X-ray mapping of the sample surface to study the elemental composition and destruction of coal particles in the microwave field were carried out by SEM method (Hitachi TM-3000 scanning electron microscope). Electronic structure of coal was studied by electron magnetic resonance method (SE/X-2544 Bruker X-range EMR spectrometer, temperature 80 and 300 K). Samples for SEM and EMR were prepared as follows. First, original coal samples were ground in MBL-100 laboratory mill (sample 1). Second, the sample 1 then was microwave-dried for 60 and 120 seconds in the microwave oven (samples 2 and 3, respectively).

Grindability of coal after microwave drying was evaluated during analysis of its size distribution. The size of coal particles more than 50 μm was evaluated by dry fractionation on SLM-200 sieves by standard method. Measurements in 50 μm–100 nm range were carried out with CPS Disc Centrifuge instrument (Model DC 2400). Fine dispersion of samples was carried out by grinding in laboratory blender (5000 rpm, 3 min) designed on the basis of Waring 8010D (USA) instrument followed by air drying for 36 hours at 300 K.

Results and Discussion

Partial pressure of water in micropores increases with heating. Internal cracks originate; after that, macrocracks evolve and hydraulic fracturing occurs. Internal porous structure of coal changes (micropores decompose, coal shrinks after removal of moisture) [7].

Fig. 2 shows the disruption of the structure of a coal particle by high internal pressure of water vapor caused by microwave heating. The surface features ridges, planes with outlets of nanosize pores (white spots).

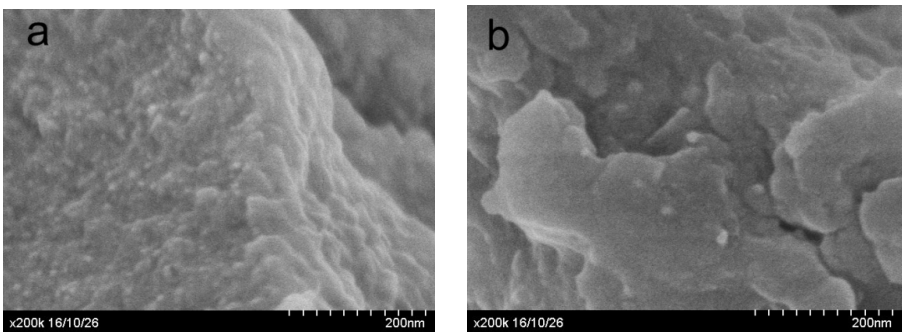

Fig. 2. (a) SEM micrograph of coal particle surface (scanning-electron microscope); (b) coal particle surface after microwave heating (sample 2). White spots in Fig. 2b are nanosized pores.

To find out how microwave heating affects the grindability of coal, the size distribution of samples has been studied. The initial sample (sample 1) is specified by bimodal particle size distribution (50 μm…3.8 μm). The weight content of finer fraction (less 50 - μm) is more than 60% of the sample's weight. Microwave drying affected grindability of coal in samples 2 and 3. Grinding of the fine fraction made the particle coagulate (Fig. 3). The width of granulometric curve decreased by more than two times, the maximum has shifted towards larger sizes (5 μm instead of 3.3 μm).

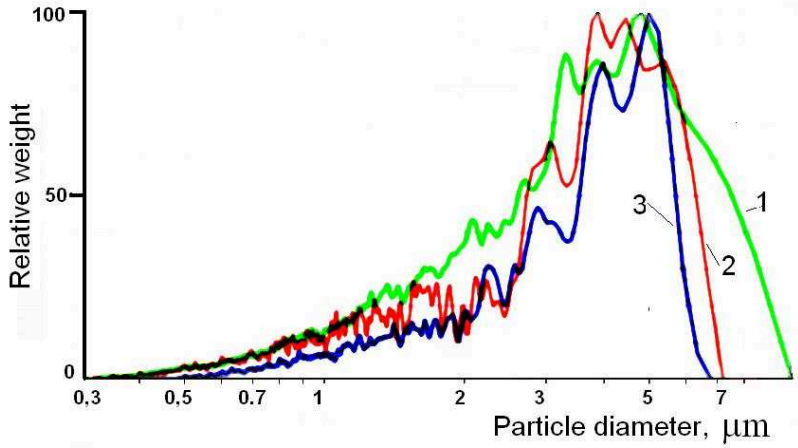

Fig. 3. Granulometric curve in 0.3-10 μm range (1, 2 and 3 are samples 1, 2 and 3, respectively)

Elemental composition was found by X-ray mapping of coal particle surface. They are C, O, Fe, S, Ca, Mn, Na, Mg, Al, Si, P, Cl, Ti, Sr, Ba. The microelements can be a part of organic part of coal or its mineral components.

EMR method applied to study the effect of microwave drying on coal makes it possible to investigate the relationship of structure and electron properties of the coal matter.

Fig. 4 shows EMR spectrum specific for all samples under study. It comprises low-field broad line L and high-field intensive narrow line R. Very weak lines of superfine structure Mn2+ (6 lines) close to the radical line are observed.

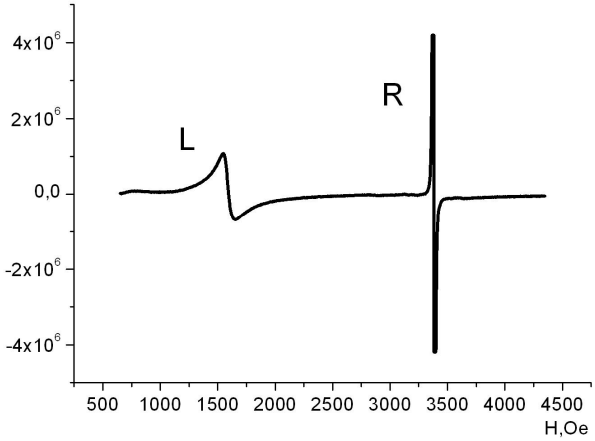

Fig. 4. EMR spectrum Kansk-Achinsk brown coal (300 K)

Line L in the domain of magnetic field 1600 Oe with g-factor about 4.27 is simulated by three Lorentz lines L1, L2, L3 (Fig. 5).

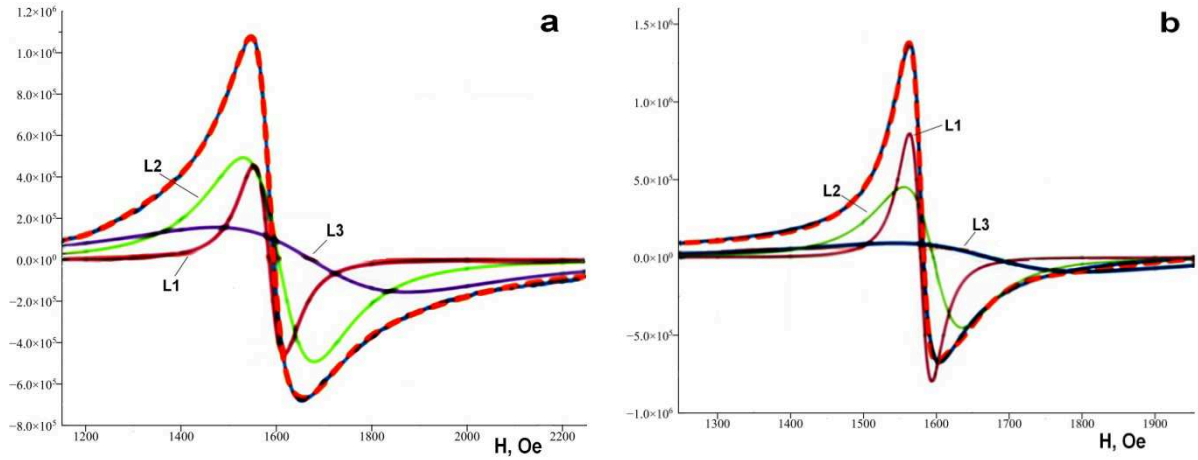

Fig. 5. Simulation of EMR spectrum by Lorentz lines (typical sample),
(a) 300 K; (b) 80 K.

Similar EMR lines were found in glass [8]. Conclusions about glasslike structure of coal were given earlier in [9, 10]. In [9] coals were considered as multicomponent organic glasses. In [10] the investigation of physical-mechanical (elastic) properties of coals disclosed their affinity with properties of glasslike solid bodies. Elemental analysis carried out in the samples under study shows presence of Al, Si, O, which form alumosilicates (clay minerals, fieldspars). In this case, the formation of oxygen tetrahedra is possible.

Line L1 is attributed to Fe3+ ions localized in oxygen tetrahedra of mineral component of coal. Line L2 corresponds to Fe3+ ions localized in oxygen tetrahedra belonging to deformed graphite-like areas of the organic component (line L2) (Fig. 1b). Line L3 is determined by Fe3+ ions localized in OPC (Fig. 1a). EMR parameters of lines L1, L2, L3 (g-factor, line width ΔH, strength I, area S) vary with microwave treatment.

G-factor is observed to increase; the width and area of the line decrease; strength of line L is observed to increase. Microwave treatment affects differently Fe3+ ions in different positions.

All samples are observed to have minimum alteration of g-factor ($g \approx 4.27$) after microwave treatment for L1. This proves the assumption that these stable tetrahedral positions of Fe3+ are associated with mineral components of coal. EMR parameters of lines L2, L3 depend on microwave treatment. The parameters of line L3, thus, depend on microwave treatment more than those of L2. This is associated with different arrangement of Fe3+ ions, i.e. with the inhomogeneity of electronic structure of organic part of coal.

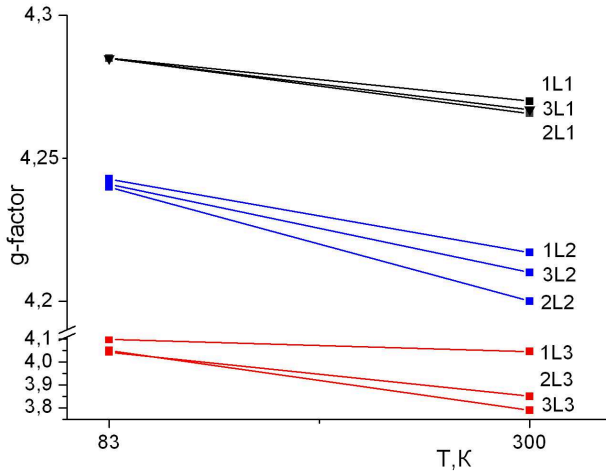

Fig. 6. G-factor of lines L1, L2, L3 for samples 1, 2 and 3

At temperature of 83 K, g-factor of lines L1, L2, L3 increases. This is explained by similar distortions of the structure around Fe3+ ions. From Fig. 6 it is apparent that degree of these deformations is different. The values of g-factor of L1 and L2 are close, this means that the structure of energy levels is approximately similar.

When cooled, the lines increase their intensities in all samples, sample 3 (L1), in particular, (Fig. 7).

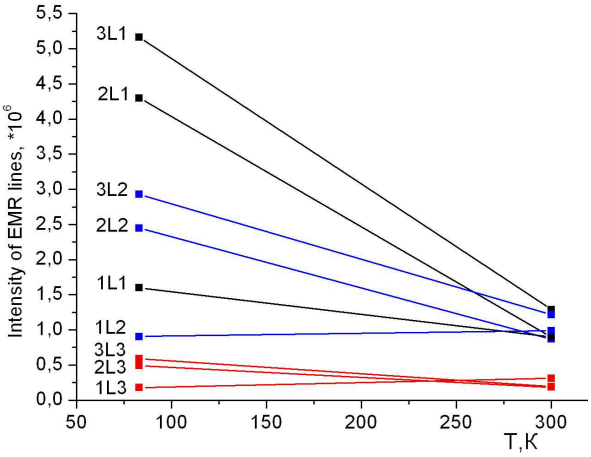

Fig. 7. Intensity of EMR lines for the samples 1, 2 and 3

This is specific for paramagnetic centers [8]. L1 and L2 exhibit the highest intensity in sample 3 and slightly less for sample 2. After microwave treatment of line L3 for samples 2 and 3 almost does not change with decrease of temperature. But, simultaneously, the intensity of L1 and L2 drastically increases, for sample 3, in particular. This can be associated with increased mobility of ions after impact of microwaves in the amorphous part of OPC and redistribution of positions of paramagnetic ions, specifically, of Fe3+, into more stable positions within oxygen tetrahedra.

Radical centers are formed by carbon atoms of carbonyl (=C=O), carboxyl (–COOH–) and phenoxy (≡C–OH) groups, hydrocarbon fragments (≡C–H) of different type. The radical line is simulated by two Lorentz lines R1, R2; this is explained by the presence in brown coals of radical centers of several types. Removal of water deeply affects the concentration and nature of radicals, i.e. the electronic structure of coals [11].

The value of g-factor for R1 and R2 is bigger than the g-factor when the electron position is fixed (g-factor = 2.002322). In this case, radical electrons of R1 and R2 are mobile.

Conclusions

The study showed that microwaves efficiently affect the structure and electronic structure of brown coal associated with it. Changes in electronic structure found by analysis of EMR spectra after exposure to microwaves make possible to trace structural changes of OPC, status of mineral part of coal. Microwave heating was found to produce movement of paramagnetic Fe3+ ions from unstable positions to the stable ones.

Acknowledgements

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References

[1] A.D. Alexeyev, Ye.V. Ulyanova, V.V. Trachevsky, L.I. Ivashchuk, S.V. Zimina, Application of Raman scattering techniques and nuclear magnetic resonance for investigation of the structure genesis of a natural carbon nanomaterials, Fizika i tekhnika vysokikh davlenii. 3(20) (2010) 126–140.

[2] P.N. Kuznetsov, L.I. Kuznetsova, S.M. Kolesnikova, Ya.V. Obukhov, Comparison of supramolecular organization of brown coal from different deposits, Chemistry for sustainable development. 9 (2001) 255–261.

[3] Y. Sun, A. Mukherjee, O. Kuznetsov, R. Thaner, L.B. Alemany, W.E. Billups, Functionalization by reductive alkylation and mappimg of a subbituminous coal by energy dispersive X-ray spectroscopy, Energy Fuels. 25 (2011) 1571–1577.

[4] Vl. Salamatov, S.E. Pashchenko, S.O. Sladkov, Vas. V. Salamatov, Application of microwaves for obtaining ground solid fuel, Journal of engineering physics and thermodynamics. 1 (89) (2016) 50–65.

[5] A.A. Khaidurova, V.V. Fedchishin, N.P. Konovalov, Microwave drying of brown coal and improvement of their technological characteristics, Izv. Vuzov. Problemy energeitiki. (1–2) (2010) 31–35.

[6] O.S. Danilov, V.A. Mikheev, T.V. Moskalenko, Microwave processing solid fossil fuels, Gorny informatsionno-analytichesky jurnal. 3 (2010) 23-31.

[7] M.Y. Ogaki, H. Usui, O. Okuma, The advantages of vacuum-treatment in the thermal upgrading of low-rank coals on the improvement of dewatering and devolatilization, Fuel Processing Technology. 84 (2003) 147–160.

[8] S.A. Altshuler, B.M. Kozyrev, Electronic paramagnetic resonance in connections between elements of intermediary groups, Nauka, Moscow, 1972.

[9] V.B. Porfiriev, Metamorphism of fossil coals, Izd. Lvovskogo universiteta, Lvov, 1948.

[10] A.A. Bely, V.I. Minayev, A.V. Podynogina, D.L. Shirochin, Deformation of coal and polymers as a subject of fractal rheology, Gorny informatsionno-analytichesky bulleten. 4 (2005) 52-59.

[11] T.V. Moskalenko, V.A. Mikheev, Mathematical modeling of electronic structure of coal, Vestnik IrGTU. 6 (89) (2014) 158 –160.