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Integrated Investigation of the Structure of Industrial Green Coke

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Abstract

Integrated studies of green coke have been carried out by means of X-ray diffractometry, electron microscopy, electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR). It is determined by EPR spectroscopy that two types of radical structures are present in the samples: low-molecular aromatic radicals and conjugated polyaromatic structures in which the unpaired electron is delocalised. Analysis of line shapes in the EPR spectra reveals differences between the green coke samples under investigation. EPR is shown to be highly sensitive method allowing one to follow the changes of molecular structure during the production of green coke. The results obtained in the work with the help of EPR are in good agreement with the results of NMR spectroscopic studies. It is concluded that evaluation of the molecular structure of intermediate coking products is necessary to improve the composition of initial raw material and technological operations.

Keywords: coke, green coke, isotropic phase, X-ray diffractometry, scanning electron microscopy, EPR, NMR, anisotropic coke, isotropic coke

INTRODUCTION

The sustainable development of heavy industry, in particular metallurgy, needs electrodes with the required electrotechnical characteristics. One of the materials for their formation is anisotropic (so-called needle-like) coke, with its economic availability, chemical purity and high electric conductivity, which makes it most profitable and highly relevant [1–3]. The main criteria for the evaluation of coke quality for its applicability in electrode materials are based on the following factors: actual density, thermal conductivity, specific electrical resistance, ash content, composition of impurities and their concentrations, crystal structure, as well as porosity and thermal coefficient of linear expansion [4, 5].

Relying on the known criteria of coke quality evaluation, one may state unambiguously that this is a complicated and multicomponent task requiring many physicochemical methods to be involved. Quality evaluation relying on only one parameter (for example, conductivity) may result in substantial errors in determining coke characteristics. It is noteworthy that coke quality is to a substantial extent determined by the choice of initial raw material, its chemical purity and the conditions of its processing and preparation for coking [6–8].

The most informative parameter determining the quality of coke for its application in electrode materials is the degree of anisotropy [9], which allows coke classification assigning the score, from 0 to 7 – from isotropic (so-called shot coke) to completely anisotropic ones (for example, needle

coke) [10]. The crystal structure of cokes determines their physical, mechanical characteristics, as well as application areas [11].

The major factor that affects the crystal structure of coke is the chemical and molecular composition of initial raw material [3, 12–16]. Substantial differences in the structures of coke samples obtained from the raw materials with the domination of definite types of organic structures, such as paraffinic, naphthenic, or aromatic, were demonstrated in [15]. For instance, anisotropic needle coke is formed from oils in which prevailing structures are paraffins, providing the growth of carboid formations in one direction during coking. A lower degree of anisotropy is observed in coke obtained from resins. These coke samples have sponge-like structure and not very high degree of anisotropy; fibrous formations are also observed in their structure. The least structured coke is formed when asphaltenes are used as the initial raw material, which results in isotropic structure arising due to the growth of dense colloidal formations uniformly in all directions.

The formation of ordered graphite-like structures during coking proceeds through consecutive detachments of aliphatic structures from the conjugated aromatic systems [17–21]. The ruptures of C–C bonds as a result of high-temperature processes take place according to the homolytic mechanism with the formation of unpaired electrons (paramagnetic centres (PMC)) on carbon atoms. With an increase in temperature, the amount of aliphatic fragments in the total organic mass decreases, while the amount of conjugated aromatic rings increases up to the formation of graphite-like structure due to recombination of aromatic radicals [22]. It is also known [23, 24] that the pyrolysis of organic mass involves the removal of the surroundings (matrix) of radicals. This finally causes a decrease in the distance between polycyclic aromatic radicals with high molecular mass and leads to the formation of bonds between high-molecular radical structures due to the dipole-dipole interaction. Investigation of the formation of radical structures in coke and green coke is extremely important for the improvement and refinement of technological stages for obtaining anisotropic coke.

The PMC formed as a result of pyrolysis may be localised on carbon atoms surrounded by protons (aliphatic radicals or low-molecular aromatic radicals) or may be delocalised over the conjugated aromatic system (high-molecular conjugated aromatic radicals). Evaluation of the nature of radical structures by EPR spectroscopy is possi-

ble with the analysis and the shape and line width of the signal observed in the spectrum [25, 26]. It is known [27–29] that the largest contribution into the line width of the EPR spectra of carbon materials is made by the spin-spin interaction between PMC localised on carbon atoms in the aromatic ring or on carbon atoms in aliphatic radicals. At the same time, the most substantial contribution into a decrease in line width is made by exchange interactions between PMC delocalised over the conjugated polycyclic aromatic system.

It is noteworthy that it is impossible to record the EPR spectra of cokes with a substantial degree of graphitisation because of their electrical conductivity (the presence of electron gas), which makes it impossible to find the resonance frequency during tuning the EPR spectrometer.

To optimise coking processes for obtaining anisotropic cokes and for improving the technological processes of coking, in addition to the studies of structural and shape-size characteristics [30], it is also necessary to investigate the structural-molecular and radical composition at different stages of coking. The optimal objects for this purpose are green cokes that may be studied using EPR and NMR spectroscopy because of their relatively low electrical conductivity.

EXPERIMENTAL

Methods of investigation

X-ray diffraction studies were carried out with a powder X-ray diffractometer Bruker D8 Advance A25 (Germany) (CuK_α -radiation, with a Ni filter on the secondary beam) at room temperature using the polycrystal method. The X-ray diffraction patterns were recorded by signal accumulation (2 s) with the scanning step of 0.02° over 2θ .

To record representative diffraction patterns, the green coke samples were disintegrated to particle size less than 0.02 mm, transferred into the cell, and pressed. Indexing of diffraction reflections was performed using the ICDD PDF-2 database [31]. Measurements of interplane spacing (d_{00l}), the thickness of polyarene packets (L_c), the density of their packing (ρ), the number (N) and longitudinal size of structural elements (L_a) were calculated according to the procedure described in [32].

The electron microscopic images of green coke particles were taken with a JEOL JSM-6390 LA scanning electron microscope (Japan). Sample microstructure was investigated with secondary elec-

trons on particles ~3 mm in size. Elemental analysis was carried out with the energy-dispersive analyser JED 2300 (Japan) with green coke particles ground to a size of less than 0.2 mm. The X-ray fluorescence spectra were recorded from the spots 1 mm² in area with the accelerating voltage of 20 kV and beam current 1 nA. The calculation of elemental composition was made using the standardless method ZAF.

The EPR spectra of green coke samples were recorded with a Bruker EMX micro 6/1 spectrometer (Germany) operating within the X band at room temperature in the air. The frequency of microwave radiation was ~9.8 GHz, the power of MMW radiation was varied from 1.9 μ W to 200 mW; modulation signal frequency was 100 kHz with the amplitude of 1 G. The concentration of PMC was calculated by comparing with the standard sample (Mn²⁺ ions doped with MgO) [33]. Simulation of EPR spectra and shape line analysis were carried out using the EasySpin software [34] in Matlab with the Simultispin graphical interface [35].

The high-resolution NMR ¹³C spectra in the solid state were recorded with a Bruker Avance III 300 W NMR spectrometer (Germany) at the frequency of 75 MHz using the standard procedure with cross polarisation and magic angle spinning (CPMAS). To obtain the quantitative data, spectra were modelled using the Dmfit software.

RESULTS AND DISCUSSION

Investigation of the structural characteristics of green coke

The XRD analysis revealed the presence of intense reflections characteristic of most of carbon

materials: 002, 004 (00 l), and a two-dimensional reflection 110 ($hk0$) in all diffraction patterns.

The detailed analysis of (00 l) reflections shows that these reflections are asymmetric with the domination of the right shoulder, which is due not only to differences in the coherent length values but also to different interplanar spacing values; this may be explained by the existence of several crystal phases in the sample. The low intensity of 004 reflection and the absence of 006 reflection indicate that the presented samples are characterised by the low degree of crystallinity. The estimated structural characteristics are shown in Table 1. One can see that the green coke samples are poorly structured, the number of polyarene layers in a packet does not exceed 11, and the parameter L_a is not more than 30 Å. Almost similar values of L_c and L_a show that nanocrystallites forming the structure of green coke are isotropic.

The isotropic structure of the samples is also confirmed by the morphology of green coke particles (an example of SEM image of green coke is shown in Fig. 1). No particles with lamellar (layered) structure characteristic of anisotropic (needle) coke are observed in the sample. The particles of all samples under investigation possess similar structural characteristics over all directions, and the structure of fractured surface looks characteristic of a vitreous amorphous body.

Investigation of the chemical and molecular composition

Analysis of the data on the elemental composition of objects (Table 2) shows that the largest amount of carbon and correspondingly the smallest amount of hydrogen is observed in sample 1. Quite contrary, the smallest amount of carbon is observed in sample 3. In addition to carbon, hy-

TABLE 1
X-ray structural parameters of the samples under investigation

Structural parameter	Sample							
	1		2		3		4	
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
d_{002} , Å	3.436	3.512	3.435	3.500	3.439	3.499	3.432	3.486
L_c , Å	31	16	34	20	32	17	32	17
Fraction of phase	0.3	0.7	0.4	0.6	0.2	0.8	0.2	0.8
ρ , g/cm ³	2.22	2.17	2.22	2.18	2.22	2.18	2.22	2.19
N , sp.	10	6	11	7	10	6	10	6
L_a , Å	29	22	30	24	28	22	28	22

Note. d_{002} – interplanar spacing; L_c – packet thickness; ρ – packet packing density; N – number of packets; L_a – Longitudinal size of structural elements.

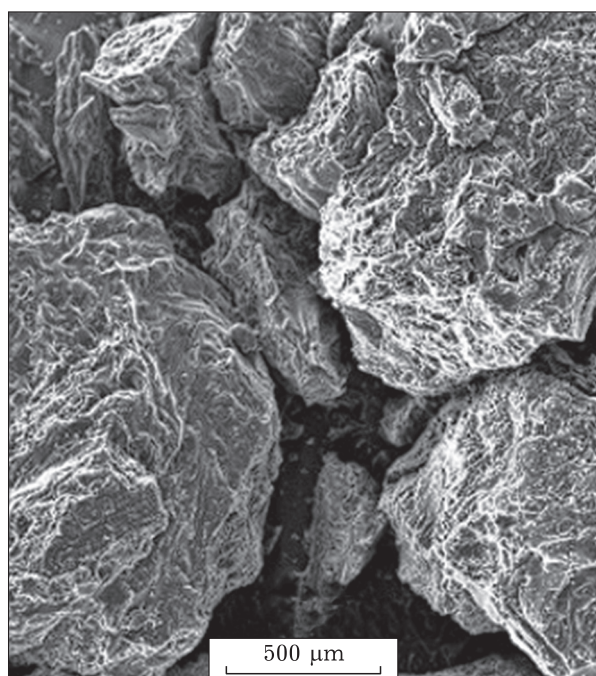


Fig. 1. SEM microphotograph of a sample under investigation.

drogen and oxygen, trace amounts of silicon sulphur and aluminium were also detected in the samples.

The low degree of graphitisation (see Table 1) allowed us to carry out EPR and NMR spectroscopic studies of the samples. All EPR spectra of the samples under investigation (an example of the spectra is shown in Fig. 2) contain two lines with identical g -factor value: a narrow line with the width of 2–2.5 G against the background of a broad one (5–6 G). Then the effect of input MMW radiation power on the EPR signal of the samples was studied. As a result, it has been revealed that a central narrow band is observed to appear with an increase in MMW radiation power only in the EPR spectrum of green coke sample 1 (Fig. 3), while this band is not observed in the case of low power. The absence of a central narrow component in the spectrum of sample 1 is due to the overlapping of the broad and narrow spectral components because this sample possesses the smallest width of the broad component among all the studied samples. The concentration of PMC and g -factors are almost the same over the whole set of samples, as shown in Table 3.

To exclude the effect of vanadium complexes that may give a narrow line in EPR spectra [35], simulation of EPR spectra with vanadyl ion was carried out. Comparison of the experimental and simulated spectra demonstrated line mismatching (Fig. 4). So, the appearance of a central nar-

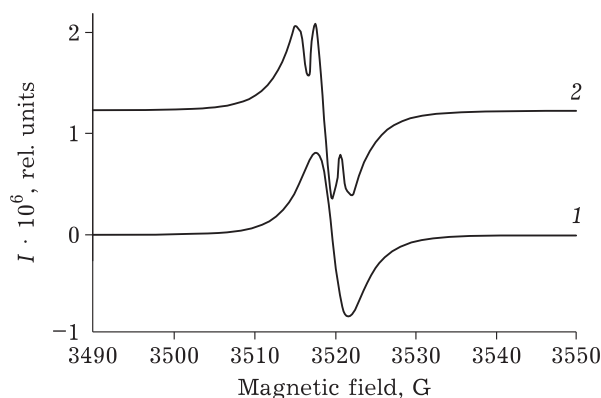


Fig. 2. EPR spectra of green coke: sample 1 (1) and sample 4 (2).

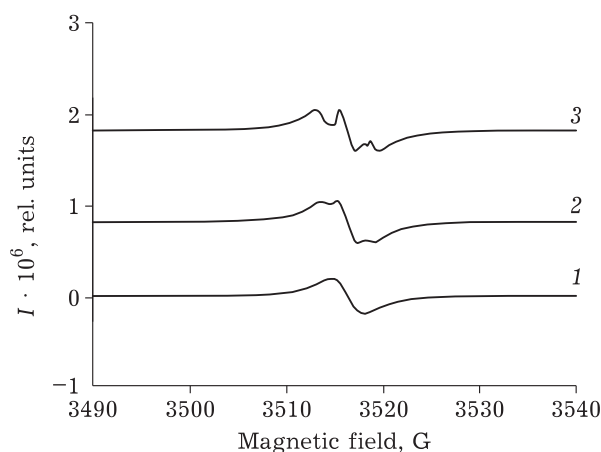


Fig. 3. EPR spectra of sample 1, recorded at different input power of MMW radiation: 1.93 (1), 3.06 (2) and 4.85 mW (3).

row line in the EPR spectrum may be related to the structural features of radicals in the organic mass of green coke.

It is known from the publications [27–29] that the major contribution to line broadening in the EPR spectra is made by spin-spin interactions of unpaired electrons localised on isolated (non-conjugated) aromatic rings. A decrease in the width of lines in EPR spectra of carbon materials is related to the exchange interactions between unpaired

TABLE 2
Elemental composition of samples

Sample	Content, wt. %				
	C	O	Al	Si	S
1	92.62	7.15	0.04	0.04	0.15
2	91.58	8.22	0.06	0.04	0.11
3	90.85	9.04	–	0.03	0.07
4	91.5	8.31	–	0.04	0.15

Note. Dash means the absence.

TABLE 3

Concentrations of paramagnetic centres (PMC) in green coke samples and g -factor values according to the data of EPR spectroscopy

Sample	PMC concentration, spin/g	g -factor
1	$1.24 \cdot 10^{20}$	2.0032
2	$1.23 \cdot 10^{20}$	2.0031
3	$9.37 \cdot 10^{19}$	2.0031
4	$1.44 \cdot 10^{20}$	2.0031

TABLE 4

Results of the decomposition of EPR spectra recorded for the samples

Decomposition	g -factor	ΔH_{p-p} , G	w , %
Sample 1			
Lorentzian-1	2.0046	3.16	49.65
Lorentzian-2	2.0029	1.79	29.49
Lorentzian-3	2.0023	2.07	20.86
Sample 2			
Lorentzian-1	2.0054	2.85	44.69
Lorentzian-2	2.0034	2.02	34.93
Lorentzian-3	2.0023	1.95	20.39
Sample 3			
Lorentzian-1	2.0058	3.12	48.92
Lorentzian-2	2.0038	1.98	31.59
Lorentzian-3	2.0023	1.95	19.49
Sample 4			
Lorentzian-1	2.0056	3.18	48.93
Lorentzian-2	2.0035	2.18	32.74
Lorentzian-3	2.0023	1.95	18.33

Note. ΔH_{p-p} – line width, measured as the distance between the extreme points on the EPR spectrum, G; w – fraction of a component in the EPR spectrum, %.

TABLE 5

Parameters of the fragmentary composition of samples according to the data of ^{13}C NMR spectroscopy

Sample	Distribution of carbon atoms over structural groups, rel. %				f_a	n
	CH_3	CH_2	Ar-H	Ar-C		
1	1.18	1.46	18.92	78.43	0.97	2.24
2	2.37	1.68	18.16	77.79	0.96	1.71
3	2.35	1.67	18.26	77.71	0.96	1.71
4	1.05	1.57	19.37	78.01	0.97	2.50

Note. f_a – aromaticity degree: $f_a = (\text{C}_{ar}\text{O} + \text{C}_{ar} + \text{CH}_{ar})/100$; n – the length of aliphatic substituents (the number of carbon atoms).

electrons delocalised over the conjugated high-molecular aromatic system. So, a narrow component of the EPR spectra of the samples under in-

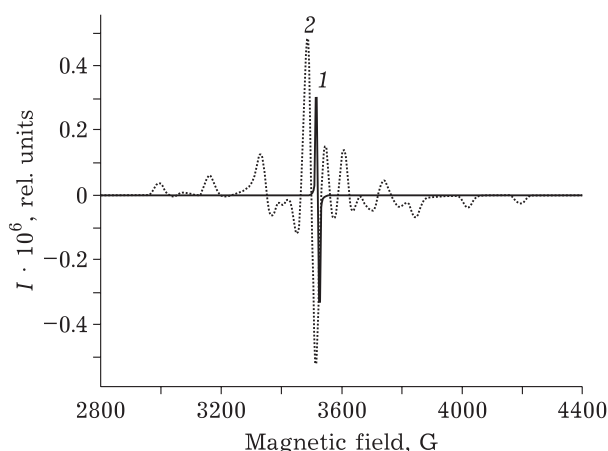


Fig. 4. EPR spectrum of sample 2 (1) recorded at 1.9 mW, and simulated spectrum of vanadyl ion with parameters: $g_{||} = 1.964 \pm 0.003$, $g_{\perp} = 1.984 \pm 0.003$; $A_{||} = 17 \pm 2$ mT, $A_{\perp} = 6.0 \pm 1.4$ mT (data from [36]) (2).

vestigation may be due to the presence of conjugated polyaromatic radicals. A broad component is due to the presence of low-molecular aromatic radicals.

Analysis of the line shape in the EPR spectra of samples (Table 4) shows that sample 1 has the smallest line width of the central narrow component, which is evidence in favour of enhancement of the role of exchange interactions between unpaired electrons delocalised on the conjugated system of polyaromatic radicals that form the packets. As reported in [28], enhancement of this effect is connected with an increase in the amount of PMC in these structures and a decrease in the distance between polyarene layers in the packets.

According to the data of NMR spectroscopy, the samples are mainly aromatic structures with a small amount of relatively short aliphatic fragments (Table 5). The smallest amount of $-\text{CH}_2-$ groups and the largest amount of carbon atoms in aromatic rings (Ar-C) are observed in sample 1. Thus, it may be assumed that shorter terminal aliphatic chains promote rapprochement of polyaromatic structures and formation of packets that are recorded by means of XRD.

CONCLUSION

It has been established by means of XRD and microscopic analysis that the samples under study are green coke with isotropic structure exhibiting almost no differences from each other in morphology and X-ray diffraction characteristics. Investigation of green coke, in particular studies of the shape-size characteristics, does not reveal

the features of physicochemical characteristics of samples in full. At the same time, it is determined by EPR and NMR spectroscopy that a green coke sample in which coking processes have taken place to a higher extent has been determined among the entire set of samples. Thus, EPR and NMR spectroscopy are informative methods to study the evolution of carbon framework formation at the stage of semi-coking.

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REFERENCES

- Meier M. W., Cracking Behaviour of Anodes, PhD Thesis, Zürich, Switzerland, 1996.
- Akhmetov M. M., Zaitseva S. A., Gimaev R. N., Production and Use of Calcined Needle Coke, TsNIITE Neftekhim, Moscow, 1983. (In Russ.).
- Niu P. X., Wang Y. L., Zhan L., Electrochemical performance of needle coke and pitch coke used as anode material for Li-ion battery, *J. Mater. Sci. Eng.*, 2011, Vol. 29, P. 204–209.
- Hume Sh., The Reactivity of the Anode, LLC Classic Center, Krasnoyarsk, 2003. (In Russ.).
- Fischer W. K., Perruchoud R., Influence of coke calcining parameters on petroleum coke quality, Proc. AIME Annual Meeting "Light Metals", Pennsylvania, 1985. P. 811–826.
- Halim H. P., Im J. S., Lee C. W., Preparation of needle coke from petroleum by-products, *Carbon Lett.*, 2013, Vol. 14, No. 3, P. 152–161.
- Predel H., Petroleum coke. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2012.
- Cheng Y., Zhang Q., Fang C., Ouyang Y., Chen J., Yu X., Liu D., Co-carbonization behaviors of petroleum pitch/waste SBS: Influence on morphology and structure of resultant cokes, *J. Anal. Appl. Pyrolysis.*, 2018, Vol. 129, P. 154–161.
- Pat. EP 2336267 A1, 2011.
- GOST 26132-84. Pitch and petroleum cokes. Method of microstructure evaluation, Izd-vo Standartov, Moscow, 1984. (In Russ.).
- Zelenkin V. G., Molotok N. P., Graphitised Electrodes for High-Power Electric Steel Making Furnaces, TsNIITsvetmet Ekonomiki I Informatsii, 1982. (In Russ.).
- Perruchoud R. C., Meier M.W., Fischer W.K., Coke characteristics from the refiners to the smelters, Proc. 129th TMS Annual Meeting "Light Metals 2000", Nashville, Tennessee, March 12–16, 2000, P. 459–465.
- Vitchus B., Cannova F., Childs H., Calcined coke from crude oil to customer silo. Tomsett, A., Johnson, J. (Eds.), Essential Readings in Light Metals, Springer, Cham, 2016, P. 3–10.
- Hals K. Production of anodes, LLC Classic Center, Krasnoyarsk, 2004. (In Russ.).
- Song S. L., Cheng X. L., The influence of alkyl group on needle coke formation, *Adv. Mat. Res.*, 2011, Vol. 335, P. 1433–1438.
- Akhmetov M. M., To the mechanism of formation of needle coke structure, *World of Petroleum Products.*, 2015, No. 4, P. 29–35. (In Russ.).
- Zhou B., Liu Q., Shi L., Liu Z., Electron spin resonance studies of coals and coal conversion processes: A review, *Fuel Process. Technol.*, 2019, Vol. 188, P. 212–227.
- Chen Y., Lee S., Tahmasebi A., Bai J., Mahoney M., Yu J., A review of the state-of-the-art research on carbon structure evolution during the coking process: From plastic layer chemistry to 3D carbon structure establishment, *Fuel*, 2020, Vol. 271, P. 117657.
- Trubetskaya A., Jensen P. A., Jensen A. D., Glarborg P., Larsen F. H., Andersen M. L., Characterization of free radicals by electron spin resonance spectroscopy in biochars from pyrolysis at high heating rates and at high temperatures, *Biomass Bioenergy*, 2016, Vol. 94, P. 117–129.
- Liu J., Jiang X., Shen J., Zhang H., Influences of particle size, ultraviolet irradiation and pyrolysis temperature on stable free radicals in coal, *Powder Technol.*, 2015, Vol. 272, P. 64–74.
- Ismagilov Z. R., Nikitin A. P., Valnyukova A. S., Mikhaylova E. S., Zaporin V. P., Galyautdinov A. G., ESR analysis of industrial needle-coke samples, *Coke Chem.*, 2019, Vol. 62, No. 3, P. 89–94.
- Xiao G., Xiong Z., Syed-Hassan S. S. A., Ma L., Xu J., Jiang L., Su S., Hu S., Wang Y., Xiang J., Coke formation during the pyrolysis of bio-oil: Further understanding on the evolution of radicals, *Appl. Energy Combust. Sci.*, 2022, Vol. 9, Art. 100050.
- Chen Y., Lee S., Tahmasebi A., Liu M., Zhang T., Bai J., Yu J., Mechanism of carbon structure transformation in plastic layer and semi-coke during coking of Australian metallurgical coals, *Fuel*, 2022, Vol. 315, Art. 123205.
- Wang W., Ma Y., Li S., Shi J., Teng J., Effect of temperature on the EPR properties of oil shale pyrolysates, *Energy Fuels*, 2016, Vol. 30, No. 2, P. 830–834.
- Xiong Z., Syed-Hassan S. S. A., Hu X., Guo J., Qiu J., Zhao X., Su S., Hu S., Wang Y., Xiang J., Pyrolysis of the aromatic-poor and aromatic-rich fractions of bio-oil: Characterization of coke structure and elucidation of coke formation mechanism, *Appl. Energy*, 2019, Vol. 239, P. 981–990.
- Semenova S. A., Patrakov Yu. F., Yarkova A. V., Lyrshchikov S. Yu., Zakharov N. S., Changes in the properties of native low-metamorphosed coal in contact with air, *Solid Fuel Chem.*, 2022, Vol. 56, No. 3, P. 157–165.
- Konchits A. A., Shanina B. D., Valakh M. Y., Yanchuk I. B., Yukhymchuk V. O., Alexeev A. D., Vasilenko T. A., Molchanov A. N., Kirillov A. K., Local structure, paramagnetic properties, and porosity of natural coals: Spectroscopic studies, *J. Appl. Phys.*, 2012, Vol. 112, No. 4, Art. 043504.
- Pilawa B., Więckowski A. B., Lewandowski M., Application of EPR spectroscopy to the characterization of magnetic interactions in thermally decomposed coal, *Magn. Reson. Chem.*, 1999, Vol. 37, No. 12, P. 871–877.
- Pilawa B., Więckowski A. B., Pietrzak R., Wachowska H., Microwave saturation of EPR spectra of oxidised coal, *Cent. Eur. J. Chem.*, 2007, Vol. 5, No. 1, P. 330–340.
- Sozinov S. A., Popova A. N., Dudnikova Y. N., Ismagilov Z. R., Structure and texture of industrial coke samples: A comparison, *Coke Chem.*, 2021, Vol. 64, No. 10, P. 451–459.
- ICDD, PDF-2 2011 (Database), Dr. S. Kalakkodu (Ed.), International Centre for Diffraction Data, Newtown Square, PA, USA.

- 32 Ismagilov Z. R., Popova A. N., Sozinov S. A., Study of coke by X-ray structural analysis and scanning electron microscopy, *J. Phys. Conf. Ser.*, 2021, Vol. 1749, No. 1, Art. 012014.
- 33 Eaton G. R., Eaton S. S., Barr D. P., Weber R. T., Quantitative EPR, Springer Science & Business Media, New York, 2010.
- 34 Stoll S., Schweiger A., EasySpin, a comprehensive software package for spectral simulation and analysis in EPR, *J. Magn. Reson.*, 2006, Vol. 178, No. 1, P. 42–55.
- 35 Molton F., Simultispin: A versatile graphical user interface for the simulation of solid-state continuous wave EPR spectra, *Magn. Reson. Chem.*, 2020, Vol. 58, No. 8, P. 718–726.
- 36 Dutoit C. E., Binet L., Vezin H., Insight into the structure of black coatings of ancient Egyptian mummies by advanced electron magnetic resonance of vanadyl complexes, *Magn. Reson.*, 2022, Vol. 3, No. 2, P. 111–124.