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IMPACT OF WEAK ELECTROMAGNETIC FIELDS ON THE PROPERTIES OF COAL SUBSTANCE

Purpose. To establish the regularities of the influence of magnetic fields on the peculiarities of changing the chemical and structural characteristics of the coal substance according to the size of microparticles enriched with vitrinite. To formulate a new system of views on the mechanisms of structural and functional transformations of coal substance under the influence of weak external fields.

Methodology. The authors used an electric furnace heating up to 320 K that creates a pulsation magnetic field with a strength of up to 4,000 A/m to process dispersed samples of hard coal with a weak magnetic field. The methods of infrared spectroscopy and electron paramagnetic resonance were used in the research.

Findings. Experimental works were carried out to estimate the impact of weak fields on the state and properties of coal substance. It is shown that weak energy fields, and the electromagnetic one in particular, are able to reduce the energy barriers of reactions in coal substance due to spin-spin interaction, which leads to the activation of processes at the atomic-molecular level and interfacial interaction.

Originality. It is experimentally established that for coal micro-particles with sizes from 0.16 to 0.1 μm , enriched with vitrinite, the coupling coefficient decreases after exposure to an external magnetic field, and for micro-particles with sizes less than 0.63 μm , this indicator increases. Such changes are caused by the redistribution of hydrogen between aromatic and aliphatic components during free-radical reactions. Changes in the spectrum on vitrinite (0.16–0.10 mm), are more significant than on inertinite (0.063–<0.05 mm). At the same time, the external action of the electromagnetic field has caused the opposite consequences. It is shown that magnetically stimulated chemical reactions occurring in the coal substance are aimed at the recombination of free radicals with active surface states of the organic mass of coal into stable gas molecules. The results of laboratory studies using the methods of electron magnetic resonance and infrared spectroscopy and infrared spectroscopy allow assuming that the changes in structural characteristics recorded during experiments with low-energy impacts can be considered as intermediators for the matter transformation or changes in the state of coal in preparation for structural and functional transformations. For example, to the sorption interaction or destructive processes with methane generation.

Practical values. The magnetic field effect can be used to develop new research methods for the study on elementary processes by electron spin resonance; control spin-dependent phase transitions. The use of magnetic resonance methods allows the usage of magnetically field effects in the form of basic tools for the research on structural defects. The results obtained will be a scientific ground for the development of methods for estimating the parameters of electromagnetic processes in coal to develop new technologies for the extraction and processing of hydrocarbon energy carriers.

Keywords: *coal substance, electromagnetic fields, structural and functional transformations, spectrum, electronic paramagnetic resonance*

Introduction. The global trend in the field of energy and environmental safety is aimed at abandoning coal as an energy carrier. Under these new conditions, a new scientific task is formulated in relation to coal – the management of the properties of coal substance and the processes taking place in it. Increased attention to the study on the properties of coals is due to the need for an adequate understanding of the conditions for the course of structural transformations, changes in the properties and state of fossil organic matter. An obvious lack of knowledge in the field of initiation and evolution of structural and functional transformations in the solid hydrocarbon matrix of natural coals is a very small amount of information about the role of weak physical fields in the processes of transformation of matter. In this regard, the relevance of fundamental research into the properties of carbonated organics is due to the insufficient level of knowledge about the essence of physical processes taking place at the nanoscale, in-

cluding those caused by the influence of weak electromagnetic fields.

Studies into the nature of fossil coals and the features of their formation make it possible to establish the general laws of the evolution of organic matter, which by its nature is poly-component, heterogeneous, and metastable. Metastability, that is, the state of quasi-stable equilibrium of a physical system, is the most important property of coal substance. The transition of such a system to a more stable state occurs under the influence of external physicochemical factors and leads to the formation of various energy-advantageous structural transformations of matter with a change in its state, properties, and composition.

Investigating the electromagnetic properties of fossil organic matter is fundamentally important in the study on structural transformations in coal substance, as it makes it possible to track and evaluate the processes in the electronic structure of macromolecules. In particular, it was established that the electrical conductivity of coal depends on the size of the aromatic nucleus of the molecule. The increase in conductivity

during the transition from coal to anthracite is explained by a significant increase in the number and mobility of current carriers, which corresponds to the ideas of delocalization and an increase in electron mobility in systems with double conjugate carbon bonds.

Electric current causes destructive physicochemical reactions in the organic component of coal [1] similar to those that take place in the rocks of the earth's crust (Nyussik, Komov, 1981; Khairtdinov, 1990; Khairtdinov, et al., 1997), including in fossil organics in the process of coalification. The treatment of carbon samples with an electric field leads to a change in the intensity of valence oscillations in different functional groups. The passage of a weak electric current initiates destructive chemical processes in coal and increases the concentration of paramagnetic centers (PMCs) in the molecular structure of the organic component of coal. The presence of oxygen-containing compounds on the surface of coal contributes to an increase in its electrical conductivity.

Peculiarities of the reaction of the structure of a carbon substance to the action of an electric field or the difference in electric potentials are associated with different charge carriers: in the case of exposure to an electric field, oriented dipoles are involved, and when the sample is in galvanic contact with a current source, the processes in the carbon matter are affected by injected electrons.

The emergence of electric fields in coal seams is also possible with the imposition of periodic mechanical influences that do not lead to destruction, due to the polarization of individual sections of the structure during their relative shifts under mechanical load, that is, as a result of the implementation of the piezo effect.

In pre-non-polarized samples of coals selected from the emission-hazardous zones of the coal seam, the existence of "natural" electric charge was discovered (Zaitsev, et al., 1992) arising from local stress metamorphism. The effect of a pulsating weak electromagnetic field on samples of non-ejector-hazardous coal leads to the accumulation of electret charge with an abnormally long relaxation time of electret potential [2]. For fossil organics, represented by two-dimensional hexagonal crystalline phases of carbon, as well as due to the entrainment of electrons by free traps associated with various defects in the structure of coal, an electret state is characteristic [3].

The reliability of the course of structural and chemical transformations of a carbon substance is determined not so much by the intensity of external action but by the type of energy that comes to the substance, as well as by the features of the molecular structure of carbonated organics. Of particular interest is the study on coal with the general influence of several low-energy factors (weak thermal, electric, magnetic fields).

Thus, studying the conditions and mechanisms of structural and functional transformations in the atomic-molecular structure of coal substance, leading to a significant change in its state and properties, is a relevant task. The development of scientific research in this area will contribute to the effective development and improvement of methods for managing the state of the coal seam, in order to improve labor safety and reduce the impact on the environment, as well as interest in improving the efficiency of coal processing and use.

Study problem statement. A realistic model of structural transformations in such a heterogeneous system as coal should be based, first of all, on reliable experimental data, as the basis for building a process model. However, studying the structural transformations of metastable coal substance is impossible in a classical theoretical-empirical way. Due to the complexity of the molecular structure of fossil coals (Gulmaliev, et al., 2003), there is a need to use an empirical-analytical method for isolating target information [3, 4]. Practical experience shows that the inflow of energy from the outside initiates space-time transformations, accompanied by a change in the physicochemical properties of a solid [5, 6].

It is known that the properties of any substance, and coal, in particular, are due to the physicochemical features of the atomic-molecular microstructure and largely depend on thermobaric, electromagnetic, and other conditions in the formation [7]. Low energy activation of transformations in a metastable substance makes it possible to cause controllable structural transformations in the solid hydrocarbon matrix of coals due to weak, in the energy sense, impacts. One of the explanations for such processes in carbonated organics may be the high content in the structure of macromolecules of the substance of paramagnetic centers $(1-4) \cdot 10^{19}$ spin/gram. The interaction of the magnetic field of PMCs or their clusters with an external magnetic field leads to an increase in spin-spin interaction. That is, in a carbon substance, spin effects are realized through free radical reactions and their catalysis. A free radical is a molecule with a dangling valence bond – with an unpaired electron, that is, a single charge capable of migrating. It is of fundamental importance that it is the place of the break that moves, rather than the physical object (Semenov, 1958). The movement of charges creates a magnetic field. Consequently, the magnetic field in coals is a consequence of free-radical processes, that is, the movement of charges in the structure of matter.

An increase in the magnetic susceptibility of the sample indicates an increase in the number of magnetic signal sources under the external influence since the magnetic susceptibility of a unit charge is constant [8]. Therefore, external and local magnetic fields can serve as a tool for controlling spin-dependent processes in the presence of a significant contribution of other driving forces of magnetically stimulated effects.

Papers on the physics and chemistry of coal lack fundamental studies into the magnetic properties of fossil organics in general or its components. There are also no clear ideas about the nature of the magnetism of carbon compounds and, in particular, fossil organics. The possibilities of assessing the influence of magnetic fields on free-radical reactions or vice versa, the formation of a magnetic field in the process of structural transformations, conformational transitions, and others, have not been clarified.

The basic parameters characterizing the magnetism of any substance include magnetic susceptibility and its anisotropy, that is, the magnitude of the connection between the magnetization of a substance and the magnetic field in this substance. It is believed that in the molecules of paramagnetic substances there are circular currents, the axes of which, in the absence of an external magnetic field, are not ordered, therefore, the magnetic field created by them is zero. When an external magnetic field is applied, the axes of these circular currents are oriented, and the magnetic field induced by them creates tension.

The review article by Makarova (2004) gives research data on the main types of carbon structures for which magnetic properties are inherent: carbon structures containing trivalent elements, for example, P, N, B; structures that are a combination of sp^2 - and sp^3 -coordinated carbon atoms; graphite, single-layer, two-layer, and three-layer graphene [9]; chains of interacting radicals; fullerenes. The study into the transformation of graphene into a polyatomic linear chain was carried out by field emission microscopes [10, 11]. Analyzing electron images of molecular orbitals of chains, the authors showed that the sequential breaking of chemical bonds and chain pulling provides an induced excess charge localized at the end of the chain. It is the localized charge that creates the axial load $(3.5-5.2) \cdot 10^{-9}$ N. In [12], the authors proved that the breaking of bonds is accompanied by local heat release, while the amplitude of atomic oscillations corresponds to a temperature of 10^4 K. This order of temperature contributes to the separation of the chain from graphene, regarding the stability of which the theory [13, 14] predicts its decay if the number of atoms has not exceeded some critical value. Based on modern ideas about the structure of coal [5],

it can be argued that four of the five carbon structures noted in the review, which are inherently magnetized, are part of the macromolecules of coal.

The magnetic properties of graphite are determined mainly by the circular currents circulating between the flat layers. Cyclic delocalization of electrons in aromatic compounds directly affects the magnetic properties, changing diamagnetic susceptibility: that is, the external magnetic field induces a diamagnetic ring current. In addition, graphite, containing certain kinds of defects, is capable of spontaneous magnetization (Makarova, 2004). In this case, defects caused by the capture of hydrogen atoms by carbon structures also lead to an increase in magnetic properties. At the same time, the time of presence of oxygen negatively affects the magnetic properties of the coal substance.

Mechanical action can change the magnetic properties of carbon structures. Under conditions of mechanical compression in macromolecules of natural copolymers, a correlation occurs between the spins (a magnetically ordered phase occurs), therefore, the magnetic properties of carbonized organics are formed (Makarova, 2004).

The mining and geological conditions in which the structure and energy state of the coal substance were formed and are formed affect its magnetic properties, namely the magnetic susceptibility of coal [7, 15]. The study into the dependence of the energy characteristics of the magnetic field on the external influence of physical factors makes it possible to investigate the kinetic parameters of the processes in the molecular structure of the coal substance associated with the macroscopic properties of coal. Geological processes, accompanied by an increase in pressure and temperature, affect the state, composition, and properties of coal [16, 17]. The absorption of energy by coal substance leads to transformations of its molecular structure, resulting in the structural adjustment of coal substance with the possible release of methane [15, 18]. The use, in conducting studies on the structure and properties of coal substance, of modern physical methods (NMR, EPR, ICS, KR, etc.) has significantly expanded the understanding of the conditions and mechanisms of transformations taking place in fossil organics [5, 6].

Exploring the magnetic properties of coal is certainly associated with the processes taking place in the electronic structure of macromolecules of fossil organics [18, 19], which makes it possible to refine the mechanisms and conditions for the course of physicochemical transformations and mechanochemical reactions in coal substance.

Different types of input energy lead to two different directions of transformations in the molecular structure of the coal substance. Based on the formed ideas regarding the molecular structure of the coal substance, as well as the free-radical nature of the chemical processes occurring in it, the main consequence of the mechanical effect on the molecular structure of coal samples is the homolytic rupture of covalent bonds. In this case, the formation of new free radicals occurs, that is, structural fragments of macromolecules that have an unpaired valence electron. With the relaxation of stresses, there is a migration of free valence (charges) – an electric current which is the source of the magnetic field, that is, the magnetic properties of carbon are associated with the presence of various radicals in the structure.

The second direction of structural transformations in coal substance can be associated with a magnetic signal – this is the movement of polarizable conformational defects of conjugate bonds. Mechanical load contributes to the compaction of matter and the coordination of the spatial structure of carbon chains. When the load is removed, the microstructure of the substance tends to reduce the stress by optimizing the structure by conformational transformations, that is, the migration of polarizable conformational defects. The passage of current (the movement of charges) through the medium is accompanied by a magnetic action, while the delocalization of elec-

trons in aromatic compounds directly affects the magnetic properties [20].

In the process of transformations under external influence, the formation of covalent bonds is also possible – the “annihilation” of free radicals of two different hydrocarbon chains. In this case, there is a “cross-linking” between the chains, and a three-dimensional structure of the coal substance is formed, whose development with the growth of coalification is a generally recognized fact.

It follows from the review of the above data that the magnetic signal in carbonated organics is of nature and is associated with physicochemical transformations in the molecular structure of coal (free radical reactions and conformational defects of conjugate systems). Thus, the magnetic properties of carbonated organic matter are mainly determined by the polarization of spins and ring currents, that is, carbon structures with magnetization either have a highly oriented structure or a high concentration of unpaired electrons (Makarova, 2004).

The increase in magnetic susceptibility (the energy characteristic of a magnetic signal) is a consequence of the accumulation (under external influence) of energy in the molecular structure of the coal substance. Relaxation in the substance of stored energy occurs spontaneously in the form of structural transformations associated with a change in the state of matter, in particular, magnetic properties. Moreover, the change in magnetic properties under the conditions of the isothermal-isochoric process is identical to the change in free energy (Vonsovsky, 1971). At the same time, changes in the molecular structure of matter under the thermal, mechanical influence, or the influence of electromagnetic fields in laboratory conditions are similar to coalification transformations in fossil organic matter.

External force and electromagnetic fields cause perturbation of fragments of the electronic structure of coal with the subsequent redistribution of accumulated energy in the molecular structure of matter. The decrease in the accumulated additional energy over time confirms the relaxation nature of structural transformations in the process of coalification, the consequence of which is the release of methane and the structuring of the solid phase [8].

The magnetic field is able to change the spin state only in those radical pairs for which the energy difference between the singlet (*S*) and triplet (*T*) states is comparable, as was shown in the works by Buchachenko (2001). The convergence of paramagnetic particles in the T-state prohibits the further formation of a stable molecule and the establishment of a covalent bond between the particles in accordance with the Pauli principle. A stable molecule in the singlet state can only be formed from the *S*-state of the predecessor pair. However, if the pairs are born mainly in the T-state, then with the help of a magnetic field it is possible to change the orientation of one of the spins in relation to the other. In this case, the magnetic field chooses among the physical and chemical reactions of conversion with low activation energy based on the spin state of electrons and stimulates the recombination or emergence of radical pairs. Thus, the role of the magnetic field in the structural and functional transformations of the matter is to initiate spin transitions in the cluster at the time of its stay in the excited state and the subsequent transition of the cluster to a more energy-advantageous configuration [21].

The purpose of this work is to propose a new system of views on the mechanisms of structural and functional transformations of coal substance under the influence of weak external fields.

The idea of the current work is to use the low energy activation of structural transformations to study structural and functional changes in the organic component of coal substance under the influence of weak influences.

The study materials and methods. The results of studies into the influence of electric and magnetic fields of weak intensity on phase transitions and transformations in the microstruc-

ture of coals were reported, for example, in [22, 23]. The results of the experiments indicate that the passage of a weak electric current initiates chemical reactions of the type “solid phase → gas” in coal, increasing the concentration of mobile components. In coals with a large number of aliphatic chains (low degree of carbonification), under the influence of an electric field, the processes of destruction of nanostructured components proceed as intensively as, for example, during thermal, mechanochemical, and radiation-chemical transformations. The influence of an external magnetic field can change the direction of the magnetic moments of electrons while stimulating the formation or completion of crystalline phases, carbon and hydrocarbon chains, and two-dimensional carbon structures (Buchachenko, 1974). It is assumed that magnetic fields of weak intensities can be used to create a stable carbon-gas system [2].

It has been experimentally established [23] that the effect of coal destruction is enhanced if even a weak electric field is applied to coal with a pre-destabilized microstructure. Paper [2] shows that mechanoactivation stimulates a complex of structural transformations and physicochemical processes in the organic mass of coal, accompanied by the evolution of hydrogen – a free radical stabilizer, an active participant, and “the energy basis for the conversion of organic matter of coals into methane and other hydrocarbon gases”. Some physicochemical characteristics of processed coal samples with a weak electric field [2], according to data by Frolkov, Fandeev, Malova, Frolkov, Frantsuzov, Sobolev (1997), and according to the results of mass spectroscopic analyses [1, 2, 23], are similar to the characteristics of emission-hazardous coals. Mechanically activated organic coal mass initiates a rapid break in bonds (Butyagin, 2006) with the formation of gases by a free radical mechanism (Buchachenko, 2001). It is assumed that the mechanisms of coal destruction, both in the case of electromagnetic activation and mechanochemical [24], can be interpreted from the point of view of the action of the thermal field (Avvakumov, 1986). In this case, in addition to experimental data, it is useful to take into consideration the results of quantum-mechanical modeling of the dynamics of an elementary chemical act [25], using field electron microscopy of observations of atomic orbitals of carbon monoatomic chains [10] and quantum theory in the study on methane content and emission hazard of coal seams [26].

The distribution of microparticles by fractions depending on the technique of treatment with external physical fields was analyzed [2]. It is shown that in reduced gas coals with a decrease in the granularity of microparticles, the iron concentration increases to the limit value corresponding to the concentration of iron in the ash. As a result of the effect of a weak pulsating magnetic field on the microstructure of pre-mechanoactivated coal, the size of microparticles increases significantly and, in general, the range of their fractional composition expands significantly. The maximum amount of absorbed heat is required for the formation of chemical compounds in mechanoactivated coals, and the minimum value – in the case of mechanoactivation with subsequent treatment with a magnetic field, which, in the latter case, may be associated with the additional implementation of spin-selective chemical reactions directly on the surfaces of coal microparticles.

In studies on the influence of a magnetic field with a strength of up to 4000 A/m on the properties of solid hydrocarbon matrices, the effect of magnetically induced sorption was discovered, proceeding with the addition of sorbate molecules along unsaturated double bonds of the sorbent with simultaneous replacement of hydrogen atoms. The mechanism of anomalous sorption in a magnetic field requires additional study but there is reason to assert that it is based on specific spin-selective reactions initiated by magnetic fields [2, 22].

To test the revealed effect of magnetically induced sorption, an additional experiment was conducted. As an object of research, fatty coal of grade “F” was used.

The mine samples taken were dried, crushed, and divided into size classes. The division into classes of coarseness makes it possible to significantly reduce the influence of the variability of the petrographic composition when using small (0.1 g) batches. The content of mineral impurities by size classes was not controlled. The coal substance prepared in this way was exposed to a weak magnetic field. The arrangement of the studied coal sample in the experimental device is shown in Fig. 1. The design of this device provides for the processing of both crushed and solid samples. In our experiments, a crushed sample of coal placed in a ceramic container is compressed by two hollow metal electrodes to a pressure of $(2-5) \cdot 10^5$ Pa, heated to a temperature of 320 ± 5 K, and exposed to a pulsating magnetic field with a strength of 3,750 A/m, a frequency of 50 Hz. The duration of processing in all experiments is 4 hours.

The rubber rings installed between the container and the electrodes are designed to block the possible flow of oxygen from the surrounding atmosphere into the zone of chemical reactions and prevent the leakage of gaseous products from this zone. An electric current passing through the coil of an electric furnace excites a pulsating magnetic field of given intensity in the coal samples and heats the coal container. DC power source B5-50 makes it possible to stabilize the current from 0 to 0.3 A and voltage from 0 to 300 V. Electrical parameters and temperature are registered continuously during operation.

To assess the effect of weak pulses of the magnetic field on the structural characteristics associated with the sorption properties of the coal substance, modern structural research methods were used – electron paramagnetic resonance (EPR) and infrared spectroscopy (IRS).

The EPR method (modernized spectrometer RE-1301) provides precision studies on structural transformations of fossil organics and also makes it possible to highlight information about the properties of the components of the heterogeneous composition of a coal substance to compare the data acquired with the results of studies by other physical methods [3].

Results and discussion. The use of EPR spectroscopy in determining the features of the electronic structure of coal macromolecules and assessing the kinetics of interaction in the coal-gas system under changing baric conditions has made it possible to devise a technique to assess the limit sorption capacity of coal matter matrices, as well as a number of effective procedures and practical recommendations. The results of the assessment of the structural characteristics of coals before and after treatment with a weak magnetic field are given in the Table.

Our analysis of the data given in the table revealed the following.

The concentration of paramagnetic centers (N^a) reflects the total content in the molecular structure of the substance of paramagnetic centers (PMCs) – unpaired electrons (free radi-

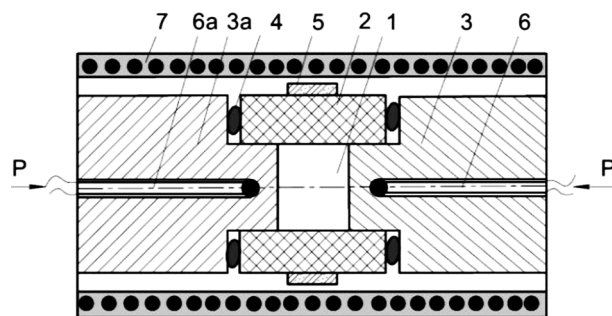


Fig. 1. Schematic arrangement of a porous sample of coal in an experimental plant:

1 – coal powder; 2 – ceramic container with working volume $V = 0.95 \text{ cm}^3$; 3, 3a – hollow steel electrode; 4 – rubber ring; 5 – copper ring; 6, 6a – thermocouple; 7 – electric furnace

Table

Results of evaluation of structural characteristics of coal substance by EPR method

Grade of size, mm	Initial state				After external influence			
	N^a	ΔH	K_{sc}	Q	N^a	ΔH	$K_{sc}Q$	Q
0.16–0.10 (enriched with vitrinite)	2.11	5.57	0.24	5.0	2.13	5.61	0.17	3.6
0.063–0.05 (enriched with inertinite)	2.11	4.32	0.26	5.6	2.27	4.43	0.37	8.4
<0.05 (enriched with inertinite)	2.70	3.86	0.46	12	2.79	3.88	0.55	15.3

icals) and defects in conjugation systems. Both types of PMCs are associated with the processes of coal-gas interaction. Sorption capacity is typically attributed to the properties of interface systems, and the processes of methane generation are free-radical in nature and take place mainly in the aliphatic component of coal substances. The indicator shows a weak upward trend.

The indicator (ΔH) is the width of the signal, depending on the nature (type) of the paramagnetic centers and the state (size) of the interface systems. The EPR spectrum of coal is the result of the overlapping of signals of two types of PMCs: narrow, belonging to the interface systems, and wide. The width of the signal also shows a weak tendency to increase associated with the nature of paramagnetism.

The conjugation coefficient (K_{sc}) is the ratio of the paramagnetic centers associated with conjugate systems to the total number of PMCs in a sample. In the class of coarseness of microparticles of coal (0.16–0.10 mm), enriched with vitrinite, this indicator decreases after external exposure. It can be assumed that in the molecular structure of vitrinite there is a redistribution of hydrogen atoms, that is, the conjugate systems of vitrinite are hydrogenated. However, at the same time, the molecular structure of inertinite (0.063–<0.05 mm and <0.05 mm) is enriched with conjugation systems – dehydrated. Both options agree well with theoretical ideas about the redistribution of hydrogen between aromatic and aliphatic components in the process of destructive free radical reactions.

Based on the data obtained by the EPR method, the limit sorption capacity (Q) is calculated. The values of the indicator are underestimated (for grade “F”) but the trends in its change after exposure are well consistent with the existing ideas about the sorption properties of coal macerals. The sorption capacity of the micro components of the inertinite group increases due to the development of aromatic cluster conjugation systems, and the sorption capacity of the macerals of the vitrinite group decreases due to hydrogenation (destruction of conjugation systems responsible for interfacial interaction).

Thus, a certain consistency in the change in structural indicators allows us to argue about the influence of weak electromagnetic pulses on the state and properties of the coal substance. However, the experiment also showed that under laboratory conditions, one weak electromagnetic effect is not enough to undergo structural transformations in an amount sufficient to significantly change the properties. Under natural conditions, electromagnetic pulses reduce the energy barrier of reactions, which is overcome mainly due to the stress energy accumulated in the atomic-molecular structure of matter. During the selection of the substance in the mine and the further preparation of samples, the stresses in the atomic-molecular structure of the coal were removed almost completely.

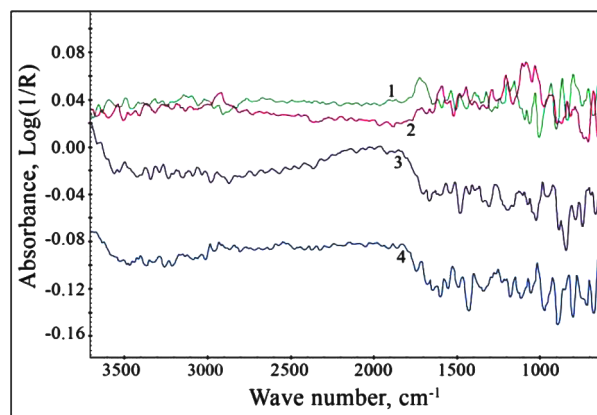


Fig. 2. Infrared spectra of coal macerals after treatment with weak electromagnetic pulses:

1 – 0.063–<0.05 mm; 2 – <0.05 mm; 3 – 0.16–0.10 mm; 4 – 0.08–0.063 mm

The use of FTIR spectroscopy (FTIR spectrometer Nicolet iS10) makes it possible to obtain information about the molecular structure of the coal matter, analyzing the features of which it is possible to assess the properties of the sample and compare the data acquired with the results obtained by other methods [5, 8].

Fig. 2 shows, as an example, the IR spectra of the size classes of coal particles before and after processing by pulses of a weak magnetic field.

On vitrinite (0.16–0.10 mm), the changes in the spectrum are more significant than on inertinite (0.063–<0.05 mm). At the same time, an external action (treatment with an electromagnetic field) led to opposite consequences on different macerals. The intensity of oscillations of interatomic bonds in inertinite has increased statistically significantly. The difference between the integral areas of the spectra before and after treatment with an electromagnetic field for the grain size class <0.05 mm is 53.339 a.u., for 0.063–<0.05 mm – 73.317 a.u.

In contrast, the treatment of grain size classes of coals enriched with vitrinite led to a decrease in the intensity of oscillations. The difference between the integral areas of the spectra before and after treatment with an electromagnetic field for the grain size class 0.16–0.10 mm decreased (–97.858 a.u.), and for grains 0.08–0.063 mm (–9.922 a.u.) decreased. One possible explanation for this fact may be the destruction of matter due to processes caused in the molecular structure by external influence.

The peak of 1,700–1,730 cm^{-1} of the oscillation of carbonyl groups increased significantly on a substance enriched with micro components of the inertinite group, especially on the grain size class 0.063–0.05 mm. Additional carbonyl groups in the treated substance appeared due to the oxidation of double bonds of oxygen in the air under external influence. A less powerful increase in the intensity of oscillations for the coarseness class <0.05 mm is most likely due to the increased content of mineral impurities in the sample. This assumption is confirmed by the presence in the spectrum of the carbon substance of the coarseness class <0.05 mm of an undisputed peak of 1,100–1,040 cm^{-1} , which is associated with fluctuations in the ash components that did not react to external influence. Increased content of the mineral component of coal is also observed in the grain size class of 0.2–0.16 mm, as peaks in the ranges of 3,600–3,700 and 1,120–1,080 cm^{-1} are associated with silicon (Si) compounds and are not indicative in these studies, as is the wide diffuse reflection peak of 2,500–3,700 cm^{-1} associated with valence oscillations of water hydroxyls.

It should be noted that in order to obtain high-quality IR spectra by the method of diffuse reflection, a prerequisite is the

comparable particle size of the substance under study, and the wavelength of the IR range. For a size class of 0.2–0.16 mm, this difference is critical, which does not allow the effective use of the substance in this state in studies.

The results of laboratory studies by EPR and IRS methods suggest that changes in structural characteristics registered in the course of our experiments with low-energy influences can be considered precursors to the transformation of matter or changes in the state of coal in preparation for structural and functional transformations. For example, sorption interaction or destructive processes with methane evolution.

The structural studies have shown that weak magnetic fields affect the structure and properties of metastable coal substance but this influence in the laboratory is not enough for a full repetition of natural transformations. Coal, as a thermodynamic system, after chipping from the seam and processing, is deprived of energy accumulated in the form of structural stresses (microstructure defects), due to which, basically, transformations take place. In the laboratory, with coal preparations in the form of finely dispersed powders being used as objects of study, weak magnetic pulses are not enough to overcome the energy barriers of reactions on a scale comparable to natural ones. In general, the trend of changes established experimentally and associated with the features of microstructural transformations and phase transitions, is close to coal in natural occurrence.

Our results can be interpreted as follows. It can be assumed that the registered effect is of a physicochemical nature and is associated with structural transformations in the atomic-molecular microstructure of carbonated organics. In our opinion, the observed nano currents are a consequence of free radical processes in the high-molecular substance of coal. A free radical is a molecule with a broken valence bond. An unpaired electron is a single charge. The movement of the charge is a current that induces a magnetic field. The possibility of moving the breaking point of the “valence migration bond has been proven (Semenov, 1958), shown for coals, and evaluated for polymers. It is fundamentally important that it is the place of the rupture that moves, rather than the physical object. This process is thermodynamically justified since this reduces the energy of the compound. Migration always occurs to the most weakened connection and contributes to its rupture, that is, the growth of entropy. In coals, there are two types of paramagnetic centers: in addition to free radicals, defects in the conjugation systems of aromatic clusters also have electronic spin. The migration of such PMCs will be the result of any conformational transitions in the carbon chain with double $C=C$ bonds. The kinetics of this process are determined by the intensity of the magnetic field. The role of the magnetic field is to initiate spin transitions in the cluster at the time of its being in an excited state and the subsequent transition of the cluster to a more energy-favorable configuration, which affects the structural and rheological properties of coal compositions. In general, the same trend of change established experimentally and associated with the peculiarities of microstructural transformations and phase transitions, is close to coal in natural occurrence.

Conclusions. The “selective” influence of the electromagnetic field of weak intensity on microparticles of coal of various granularities has been experimentally established. For example, for grains 0.063–0.05 and <0.05 mm, the sorption capacity of micro components of the inertinite group increases by 15 and ~13 %, respectively, due to the development of interface systems of aromatic clusters, and the sorption capacity of the macerals of the vitrinite group (fraction 0.16–0.1 mmm) decreases by 14 % due to hydrogenation (destruction of the conjugation systems responsible for interfacial interaction). This effect may indicate an important role of electromagnetic fields in the physicochemical transformations of coal substance in nature.

The magnetic field effect, first discovered in the organic mass of fossil coal, can be used to devise new methods for

studying elementary processes at the electron-spin level; control over spin-dependent phase transitions. The use of magnetic resonance methods makes it possible to use magnetic field effects in the form of the basis of tools for the study on structural defects.

The practical significance of the current work is related to the fact that the reported results will serve as a scientific basis to devise methods for assessing the parameters of electromagnetic processes in coal in the development of new technologies for the production and processing of hydrocarbon energy carriers.

Based on the results of experimental studies, it can be stated that a number of new effects have been established by structurally sensitive methods for diagnosing the state of metastable carbonated organic matter exposed to the action of weak electric and magnetic fields. Regrettably, the earlier discovered physicochemical transformations in the microstructure of coals [2, 22, 23] remain out of focus by scientists in the formation of ideas about the mechanisms of self-organization of solid matrices under the conditions of interphase interaction. Research advancements and extrapolation forecasts indicate the possibility of widespread use of coal resources during its deep processing. In particular, during the electromagnetic treatment of coal, destruction occurs in the fragments of the organic component of the fuel with a change in intra- and external molecular interaction, the formation of radicals, with the participation of which the acceleration of responses can occur.

The value of coal is determined not only by energy intensity but also by the possibility of concomitant extraction of compounds of a number of rare and scattered elements, methane production, as well as obtaining raw materials with high added value. Control over the state of the coal seam with the help of a magnetic field effect – its gas content and emission hazard – will make it possible to launch the processes of artificial methane evolution in coal seams and can enable the production of gaseous hydrocarbon energy carriers in the rock stratum with the release of the final product to the surface, such as the extraction of “shale” gas or oil. Currently, it is very relevant to solve problems related to the improvement of the processes of inversion of solid hydrocarbon raw materials (the hydrogen content is up to 6 % per dry ash-free mass of coal) into technologically easily implemented types of energy carriers. One of the directions in this area is the artificial acceleration of coalification, accompanied by the release of molecular hydrogen from a solid matrix with its subsequent use in the energy sector.

Thus, one of the most promising areas in the development of energy generation is the use of hydrogen as a fuel. Hydrogen is a high-calorific gas, which, in addition to energy generation, can be used in many industries. The great advantage of hydrogen is that when it is burned, only water vapor is formed, that is, hydrogen is an environmentally friendly ideal fuel. The transition to hydrogen energy generation is also promising because hydrogen is a universal energy raw material. The need for such fuel is very urgent, given that the main source of air pollution in cities are products of incomplete combustion of carbon-containing natural fuels.

The destruction of a coal substance to nanoparticles or even to an atomic state, followed by the removal of carbon in the form of soot or nano graphite and molecular hydrogen from the reaction zone, will provide a significant (to industrial levels) enrichment of the residue with nanoparticles of iron, sulfur, phosphorus, non-ferrous and rare earth metals, with the further use of practically pure elements in high-tech science-intensive processes.

Based on the studies conducted, it can be assumed that the role of the magnetic field is to initiate spin transitions in the carbonated substance at the time of its stay in the excited state and the subsequent transition of its molecular structure to a more energy-favorable configuration. It should also be noted

that the basis of the structural and functional evolution of the matrices of solid hydrocarbons is the totality of physicochemical transformations initiated by magnetic energy in a substance at different levels of its microstructure. Understanding the mechanisms and nature of the driving forces that have a fundamental influence on the phase and structural transformations of solid hydrocarbons and especially nanoscale carbon phases require new fundamental knowledge. Successful development is impossible without generalizing the results of precision measurements, quantum-mechanical modeling of surface processes, dynamics, and stability of chemical bonds, in order to formulate algorithms for non-energy-intensive and environmentally safe technologies. In this regard, it appears relevant to form a broader research program involving natural carbon-containing solid compositions in differentiating processing methods.

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Вплив слабких електромагнітних полів на властивості вугільної речовини

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Мета. Встановити закономірності впливу магнітних полів на особливості змінювання хімічних і структурних характеристик вугільної речовини за розмірами мікрочастинок, що збагачені вітринітом. Сформулювати нову систему поглядів на механізми структурно-функціональних перетворень вугільної речовини під дією слабких зовнішніх полів.

Методика. Для обробки диспергованих проб кам'яного вугілля слабким магнітним полем використовувалася електрична піч із нагріванням до 320 К, що створює пульсуюче магнітне поле напруженістю до 4000 А/м. У дослідженнях використані методи інфрачервоної спектроскопії та електронного парамагнітного резонансу.

Результати. Проведені експериментальні роботи з оцінки впливу слабких полів на стан і властивості вугільної речовини. Показано, що слабкі енергетичні поля, та електромагнітне зокрема, здатні знижувати енергетичні бар'єри реакцій у вугільній речовині за рахунок спінової взаємодії, що призводить до активізації процесів на атомно-молекулярному рівні та міжфазової взаємодії.

Наукова новизна. Експериментально встановлено, що для вугільних мікрочастинок розмірами від 0,16 до 0,1 мкм, збагачених вітринітом, після впливу зовнішнього магнітного поля коефіцієнт сполученості зменшується, а для мікрочастинок розмірами менше 0,63 мкм цей показник збільшується. Такі зміни обумовлені перерозподілом водню між ароматичною та аліфатичною складовими під час проходження вільно-радикальних реакцій. На вітриніті (0,16–0,10 мкм) зміни спектру суттєвіші, ніж на інертиніті (0,063–<0,05 мкм). При цьому зовнішня дія електромагнітного поля спричинила протилежні наслідки. Показано, що магнітностимульовані хімічні реакції, які протікають у вугільній речовині, спрямовані на рекомбінацію вільних радикалів з активними

поверхневими станами органічної маси вугілля у стійкі молекули газу. Результати лабораторних досліджень методами електронного магнітного резонансу та інфрачервоної спектроскопії дозволяють припустити, що зміни структурних характеристик, зафіксовані у процесі експериментів із низькоенергетичними впливами, можуть розглядатися як попередники перетворення речовини або зміни стану вугілля при підготовці до структурно-функціональних трансформацій. Наприклад, до сорбційної взаємодії або деструктивних процесів із генерацією метану.

Практична значимість. Магнітнопольовий ефект можна використовувати для розробки нових методів дослідження елементарних процесів електронно-спіновим резонансом; управління спін-залежними фазовими переходами. Використання магніторезонансних методів дозволяє використання магнітнопольових ефектів у вигляді основ інструментарію для дослідження дефектів структури. Отримані результати слугуватимуть науковою основою для розробки методів оцінки параметрів електромагнітних процесів у вугіллі для розробки нових технологій видобутку й переробки вуглеводневих енергоносіїв.

Ключові слова: вугільна речовина, електромагнітні поля, структурно-функціональні трансформації, спектр, електронний парамагнітний резонанс

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