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IMPACT OF SEDIMENTATION CONDITIONS ON THE COAL STRUCTURE AND PROPERTIES

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Abstract. The creation of modern methods in the complex development of coal and gas deposits is associated with the necessity to substantiate the processes that occur in fossil organics at the atomic-molecular level under the impact of natural factors, in particular for evaluating the sorption properties of coal. Actually, natural factors determine coalification processes, including methane emission from coal as well as sorption interaction between solid and gaseous hydrocarbons. Therefore, in order to study these processes, insight into the relationship between the macro properties of coal fields and features of the molecular structure of coal matter is of great importance. At present there is a large number of theoretical and experimental studies on the research of the structure and state of coal by means of various physical, physicochemical, and chemical methods. It was proved that temperature and pressure have the greatest impact on the transformation of coal matter, but there is still a number of issues that require development or revision.

The purpose of the paper is to determine the impact of sedimentation conditions of coal-bearing deposits of the Donetsk basin on the coal structure and properties.

The study of changes in the molecular structure of coal at the nano-scale is carried out by the electron paramagnetic resonance method (EPR). The concentration of paramagnetic centers (PMC, Na) is determined, i.e. the number of unpaired electrons (free radicals), the conjugation coefficient (K_{sc}), which describes the fraction of conjugated systems in the molecular structure of the coal matter and also makes it possible to evaluate the structuring degree for fossil organics at the molecular level. In order to simplify data processing and its assessing as well as reducing the variability of impacts in the research of sedimentation conditions on the structure and properties of coal, the study involved the coal of the same age (suite C_2^6) and grade (F – fiery, M – medium volatile coal). It is established that the continuous deformation of tectonic blocks over a long period of time leads to successive compaction (loosening) of a heterogeneous massif, number of defects increasing as well as changes of structural parameters and activation of coal matter. It is proved that the increased reactivity of coal causes the possibility of structural transformations at the atomic and molecular level, in particular, end-groups detachment along with formation of hydrocarbon gases, which leads to conjugation coefficient increasing for fossil organics (which, as a result, leads to the coal sorption capacity increasing).. Periodic temperature increasing of sedimentary deposits, which is associated with magmatic processes, has increased the number of paramagnetic centers and made steady their concentration in the coal matter. It is noted that the use of a thermodynamic approach and concepts of mechanochemistry to study the conditions for the coal fields formation allows researching the relationship between the properties of coal matter at the macro- and nano-scale.

Keywords: coal, geological factors, sedimentation conditions, EPR spectroscopy, molecular structure.

Introduction. Problems of modern methods creation for the integrated development of coal-gas fields are associated with the lack of proved insights into the processes that occur in fossil organics at the atomic and molecular level under the impact of natural factors, in particular, for evaluating the sorption properties of coal. Since exactly natural factors cause the coalification processes, including the methane emission from coal and the sorption interaction between solid and gaseous hydrocarbons, information about the link between the macro properties of coal fields and the peculiarities of the molecular structure of the coal matter is of great importance for the studying of these processes.

When comparing the geological conditions of different fields, certain factors that provide transformation of organic matter have been considered: paleotemperature conditions, geostatic pressure, and mineralogical composition of the host rocks [1]. Based on these materials, the following conclusions have been made: paleotemperature causes a series of successive transformations in the molecular

structure of organic matter, each of which occurs only under certain thermodynamic conditions; geostatic pressure does not significantly affect transformation of organic matter. Regarding the role of the mineralogical composition of host rocks as well as geological time, the researchers' opinions are ambiguous ones, and most believe that their influence is insignificant. But there is no doubt that under real geological conditions coalification organics are simultaneously affected by a whole complex of factors that vary in space and time, therefore an unambiguous interpretation of the results is impossible. Thus, the interpretation of the data regarding the impact of sedimentation conditions on the transformation of coal matter at the nano-scale and the formation of its properties is ambiguous and contradictory ones.

In the process of deformation and destruction of coal matter under the impact of geomechanical factors, a significant evolution of its structure takes place, and every stage of this evolution complies with array of distinguished laws. Further, the system determines the main law for every stage from the array in arbitrary manner.

The only common feature of the any factor's influence (or number of factors) on the system, which represents the coal bed, is a change of the energy state, that could be approximately estimated by the functions and parameters of thermodynamics. Given the structural and chemical diversity of organic species in coal as well as corresponding number of possible chemical reactions and transformations they are involved in, a detailed analysis of the thermodynamic aspects of the transformation for the coal organic mass structure is not possible. However, a generalized thermodynamic approach could be applied.

The main problems of the the general trends research in the development of coal transformations appear when geological macrofactors, physical and mechanical properties of rocks as well as processes, complied with quantum mechanics laws at the nano-scale, got combined. Such a combination of different scale levels in the research is possible only in line with the principles of thermodynamics through the integrating factor, i.e. energy or the energy state of the system. Thus, the study of the coal restructuring processes at the atomic-molecular level should origin from the transformation kinetics research and the parameters of the processes that occur in the coal after the equilibrium of the system was disturbed.

Under natural conditions, coal is in a thermodynamic equilibrium state due to equal-component stress. For these conditions, the activation and development of physicochemical transformations in a high-molecular organic species might occur only due to the transfer of the accumulated energy of structural stresses to the activation energy of chemical reactions. But the chemical reactions do not take place in coal particles, since the mobility of reactive complexes in a solid species tends to zero, while the chemical reaction rate depends on the concentration of reacting species. So, the main mechanism of structural transformations in coal matter is a free-radical one. First of all, free-radical reactions require much less energy, which necessary amount could be accumulated in the form of structural stresses of a mechanical or thermal nature. Further, free-radical reaction rate depends on the number of active complexes (free radicals), which remains almost constant for chain reactions.

Electron paramagnetic resonance is an effective method of high-molecular compounds studying of an unknown structure that contains unpaired electrons. It allows to obtain information not only about the chemical structure of paramagnetic centers and their environment but also about the processes that take place in the electronic structure of the species. EPR spectroscopy is important for studying the properties and state of carbonaceous fossil organic species as a way to visualize processes in coal matter.

The EPR method is based on the effect of resonant absorption for an energy sample of the ultra-high-frequency field by paramagnetic centers and appears to be the most sensitive method among spectroscopic ones because it captures information that concerns the paramagnetic part (electronic structure) of a species alone. This limitation is usually considered a disadvantage of the method, but for coal, which is a powerful paramagnet, this feature turns out an important advantage, which allows direct monitoring of the interaction of paramagnetic centers alone. Thus, it allows to study transformation kinetics at the nano-scale in the atomic-molecular structure of the coal-gas compound almost without external impacts or side effects. In addition, a significant advantage of the EPR method implies the requirements for sample preparation should be barely present, which is crucially important for the research of natural high-molecular compounds in a metastable state and, accordingly, provides the opportunity to evaluate the impact of macrofactors on the atomic-molecular structure of coal. This allows to study the impact of natural factors at the nano-scale of the matter structure.

To date, there is a sufficiently large number of theoretical and experimental papers devoted to the research of the coal structure and state by various physical, physicochemical, and chemical methods. It was substantiated that temperature and pressure are the main parameters that exert an impact on the transformation of coal matter, but there is still a number of issues that require development or revision.

The purpose of the paper is to determine the impact of the sedimentation conditions of coal-bearing deposits of the Donetsk basin on the structure and properties of coal.

Methods. The research method. The study of changes in the molecular structure of coal at the nano-scale was carried out by the electron paramagnetic resonance method (EPR). According to the elaborated methods [2], the concentration of paramagnetic centers (PMC, N^a) was determined – the number of unpaired electrons (free radicals), the conjugation coefficient (K_{sc}), which describes the fraction of conjugated systems in the molecular structure of coal matter, and also makes it possible to evaluate the structuring degree for fossil organics at the molecular level. In order to simplify data processing and its assessing as well as reducing the variability of impacts in the research of sedimentation conditions on the structure and properties of coal, the study involved the coal of the same age and grade. The results processing of the study was carried out using the mathematical statistics methods.

Results and discussion. Analysis of the obtained results. The Middle Carboniferous deposits of the diamond suite (C_2^6) are the object of the research. Suite C_2^6 is a highly cycled one with an abrupt change of facies along the suit's section. The suite section, as a whole, is lithologically stable and the cycles are usually clearly traced over the entire area of the basin. The thickness of the suite varies in the west-to-east direction from 150 to 400 m i.e., the coal seams of the diamond suite could be distinguished by the stable accumulation conditions. This is confirmed by petrographic research performed for samples that have been taken in different places of the basin from the suite's coal deposits. The results of the research are shown in Table 1.

Table 1 – Maceral composition and structural parameters for coal of F – M grade of the diamond suite

Deposits' location	Mine's name	Content of petrographic components*, %				Concentration of paramagnetic centers N^a, gr^{-1}	Conjugation coefficient value $K_{sc,}$ %
		V_t	S_v	I	L		
Western slope of the Vovchansk syncline	Pioner	79	3	7	10	1.81	56
	Dobropilska	84	2	5	9	2.18	47
	Named after O. H. Stakhanov	76	2	10	12	1.7	48
Eastern slope of the Vovchansk syncline	Lidiievka	82	2	9	11	3.6	49
	Named after O. F. Zasiadko	83	-	12	5	3.3	45
Horlivska anticline of Donbass	Komsomolets	87	4	7	2	2.4	65
	Named after V. I. Lenin	94	2	3		4.1	70
	Named after Yu. O. Haharin	84	1	11		2.8	71
	Named after M. I. Kalinin	71				3.1	57
Northern puckering zone	Named after Illich	81	2	8	8	3.0	45
	Named after the XX Congress	82	5	11	1	2.3	68
		86	2	8	8	2.3	59
	Named after V. R. Menzhynskyi	82	1	1	16	1.8	54.6

*V_t – vitrinite, S_v – semivitrinite, I – inertinite, L – liptinite.

Data set represented in the Table 1 shows that the maceral compositions of coal are the same, i.e. the phytogenous rock and paleobotanical conditions for the accumulation of sediments are the same as well. In general, the average values of K_{sc} for all areas of the basin are similar that proves that coal structuring is approximately of the same degree. But the lowest structural indicators are inherent ones for coal at the eastern slope of the Vovchansk syncline, the highest concentration of paramagnetic centers could be found in coal within the seams of the Horlivska anticline, while the highest values of conjugation coefficients could be determined for

coal of the Northern puckering zone of as well as Horlivska anticline. Wide range of structural indicators for the coal of the studied mines could be observed due to different tectonic conditions or heat flows applied for the processes of deposit formation.

In order to characterize the temperature conditions, the following parameters were used: geothermal gradient (t_{grad}) [3], a map of heat flows [4] as well as accumulation rate of sediments in carbon [4] (Table 2). Taking into account that both folded and disjunctive faultings reflect conditions of paleopressure; amplitudes of recent displacements reflect actual dynamic conditions, therefore indicators applied are able quantitatively assess these parameters. In paper [5], the methodology and data that allow to calculate indicators that describe the intensity of general tectonic dislocation (K_d) for locations of research and the intensity of recent displacements (ΣA) are given.

A comparison of indicators for different locations made it possible to determine the impact of local thermodynamic conditions on the structure of coal.

Table 2. – Indicators of thermal and tectonic conditions for the formation of coal deposits

Deposits' location (number of samples)	Geothermal gradient, °C/km	Coefficient of general tectonic dislocation (Kd)	Accumulation rate of sediment in carbon, m/mln. year.	Heat flow, mW/m^2	Amplitude of recent displacement (ΣA), mm	Average concentration of paramagnetic centers for the location, N^a, gr^{-1}	Average conjugation coefficient for the location K_{sc}, %
Western slope of the Vovchansk syncline (20 samples)	2.99	0.08	115	60	1.26	2.3	48.3
Eastern slope of the Vovchansk syncline (24 samples)	3.77	0.16	220	75	3.97	3.5	54.7
Horlivska anticline of Donbas (21 samples)	3.81	0.45	250	80	5.57	2.9	58.5
Northern puckering zone (18 samples)	1.94	0.40	195	50	3.71	2.0	59.2

The highest pressure values, both for the accumulation of sediments, the formation of tectonic dislocations as well as for the present stage of formation, was experienced by the coal of the Horlivska anticline. For the slopes of the Vovchansk syncline, especially for the western one, the activity of tectonic processes is lower than that of the Horlivska anticline. The average values for coal conjugation coefficients of the Horlivska anticline and the Northern puckering zone are higher than that ones for the western slope of the Vovchan syncline (48.3%). The data obtained could be explained by the impact of tectonic conditions on the coal

structure. The continuous deformation of tectonic blocks over a long period of time leads to the successive loosening of a heterogeneous massif, number of defects increasing as well as changes of structural parameters and activation of coal matter. An increased coal reactivity causes the possibility of structural transformations at the atomic-molecular level, in particular, an increasing of the capacity for conjugated systems in the molecular structure of the coal matter. Therefore, structuring degree of in coal seams of the Horlivska anticline and the Northern puckering zone is higher than that one for the slope of the Vovchansk syncline, which leads to an increase in the flaws of a coal matter and, as a result, to an increasing of sorption capacity.

It is obvious that the values of heat flow and temperature gradients for the western slope of the Vovchansk syncline as well as for northern Donbas are smaller than than that ones for the eastern slope of the Vovchansk syncline and Horlivska anticline. These features could be explained be explained by the difference in magmatic activity. Three magmatic cycles at the post-inversion stage were outlined in paper [4] for the eastern slope of the Vovchansk syncline. The rocks of these cycles outstand everywhere along the southern flank of Donbas. Deposits and dikes of igneous rocks are encountered in the mine workings of the “Petrovskvuhillia State Enterprise” located near the “Lidiievka State Enterprise” mine i.e., the seam at the “Lidiievka State Enterprise” mine has been heated up periodically. As a result the coal matter was subjected to all transformations possible under these conditions, and now coal is tied up. (its structure barely changes). At the same time, similar magmatic cycles have not been noted for the western slope of the Vovchansk structure, the coal matter "breathes", therefore its parameters change over time. It means that even marginal external impacts in any way (energy flow of any kind) lead to a change of the state, properties and composition of coalification organics. This is confirmed repeatedly by the results of the measurements, which were carried out for the same samples during a ten-year period. It was at this mine that The structural parameters of the coal from this mine have barely changed, while for other mines, the structural parameters of coal fluctuated within 30% range. Heating processes have the greatest impact on the concentration of paramagnetic centers. Under similar conditions of sediments accumulation, it is most likely that their subsequent periodic short-term heating led to a distinguished structure formation of molecular coal matter. For instance, this such kind of a structure consistently elucidates deviations from Hilt's law for coals from Donetsk region related to the reaction of the structure of the coal matter to changes of thermodynamic conditions.

Conclusions. Thus, under similar conditions of sediment accumulation, the structural properties of coal have changed under the impact of external thermodynamic processes. Pressure has predominantly affected the conjugation coefficient, while temperature has affected the number of paramagnetic centers.

In general, the study of the impact of tectonic forces on the structure of coal for different scales has revealed the following features:

– continuous, long-term deformation of tectonic blocks leads to successive compaction (loosening) of the heterogeneous rock massif, an increase of flaws

number as well as change of structural parameters and activation of coal matter. The increased reactivity of coal determines the possibility of structural transformations at the atomic-molecular level, in particular, the detachment of end-groups detachment along with formation of hydrocarbon gases, which leads to conjugation coefficient increasing for fossil organics (which, as a result, leads to the coal sorption capacity increasing);

- the periodic increase of sedimentary deposits temperature associated with magmatic processes has led to an increased number of paramagnetic centers and make their concentration stabilized in the coal matter;

- the use of a thermodynamic approach and concepts of mechanochemistry to study the conditions for the coal fields formation allows researching the relationship between the properties of coal matter at the macro- and nano-scale.

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ВПЛИВ УМОВ ОСАДКОНАКОПИЧЕННЯ НА СТРУКТУРУ ТА ВЛАСТИВОСТІ ВУГІЛЛЯ

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Анотація. Створення сучасних методів комплексної розробки вугільно-газових родовищ пов'язане з необхідністю обґрунтування щодо процесів, які відбуваються у викопній органіці на атомно-молекулярному рівні під дією природних чинників, зокрема з оцінки сорбційних властивостей вугілля. Саме природні фактори обумовлюють процеси вуглефікації включно з виділенням метану вугіллям та сорбційною взаємодією між твердими та газоподібними вуглеводнями. Тому для вивчення цих процесів принципово важливе розуміння взаємозв'язку макровластивостей вугільних родовищ з особливостями молекулярної структури вугільної речовини. Натепер існує достатньо велика кількість теоретичних і експериментальних робіт з дослідження структури і стану вугілля різними фізичними, фізико-хімічними та хімічними методами. Обґрунтовано, що

найбільший вплив на перетворення вугільної речовини мають температура та тиск, але досі залишається низка питань, що потребують розвитку або уточнення.

Мета роботи - визначення впливу умов осадконакопичення вугленосних відкладів Донецького басейну на структуру та властивості вугілля.

Дослідження змін в молекулярній структурі вугілля на нанорівні проводилось методом електронного парамагнітного резонансу (ЕПР). Визначалася концентрація парамагнітних центрів (ПМЦ, Na) – кількість неспарених електронів (вільних радикалів), коефіцієнт спряженості (Ksc), що характеризує відсоток систем спряження в молекулярній структурі вугільної речовини, а також дозволяє оцінити ступінь структурованості викопної органіки на молекулярному рівні. Для спрощення обробки та інтерпретації даних і зменшення варіативності впливів дослідження умов осадконакопичення на структуру та властивості вугілля проводились на вугіллі одного віку (світа С26) та однієї марки (Г – Ж). Встановлено, що безперервне, протягом тривалого часу, деформування тектонічних блоків призводить до послідовного ущільнення (розущільнення) неоднорідного масиву, зростання кількості дефектів та зміни структурних параметрів і активації вугільної речовини. Доведено, що підвищена реакційна здатність вугілля обумовлює можливість структурних перетворень на атомно-молекулярному рівні, зокрема, відрив кінцевих груп з утворенням вуглеводневих газів, що приводить до підвищення коефіцієнту спряженості викопної органіки (і як наслідок збільшення сорбційної здатності вугілля). Періодичне збільщення температури осадових відкладів, що повязане з магматичними процесами, підвищіло кількість парамагнітних центрів і стабілізувало їх концентрацію у вугільній речовині. Зазначається, що використання термодинамічного підходу та уявлень механохімії до досліджень умов формування вугільних родовищ дозволяє вивчати зв'язок між властивостями вугільної речовини на макро- і нанорівнях.

Ключові слова: вугілля, геологічні фактори, умови осадконакопичення, ЕПР-спектроскопія, молекулярна структура.

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