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Influence of Oxidability of Carboniferous Coals from the Dobrudja Foredeep on Vitrinite Reflectance

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Abstract—Importance of the study of the influence of coal oxidability on vitrinite reflectance (VR) as a criterion of the quality of coals and indicator of paleogeothermal regime is shown. Overview of relevant concepts demonstrates that this issue remains debatable. Carboniferous coals of the Dobrudja foredeep, which belong to the class of helitolites in terms of their microcomponent composition, were studied. They were subjected to oxidation during storage outdoors. Consequently, the VR value of high volatile bituminous (long-flame and gas ranks, according to the Russian classification) coals decreased, but this parameter remained virtually unaltered for medium volatile bituminous (fat) coals. Bulgarian researchers obtained similar results for Carboniferous coals of the Dobrudja basin represented by helitolites and mixtohumolites. In our opinion, the VR decrease in the course of coal oxidation is caused by decrease in the condensation and density of aromatic structures and increase in the share of nonaromatic carbon atoms.

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Investigations of oxidized coals are of scientific and practical significance, because they make it possible to understand structures and properties of coals, elucidate the causes of their spontaneous ignition, and solve the problems of their rational utilization. Therefore, interest to the influence of oxidability of coals on the VR parameter as an essential criterion of their quality is quite natural.

The issue of VR variation due to long-term atmospheric influence on coals is far from being solved. Suggestions concerning this issue are very different and often contradictory. Most of the researchers believe that coals stored for a long time under atmospheric conditions are subjected to alterations that are detected in the course of their petrographic investigation (the appearance of wedge-shaped weathering fissures and leaching cavities, disintegration, smoothing of relief, development of texture in vitrinite, and so on). Manifestation of these features is variable in style and intensity in various components and differently metamorphosed coals (Eremin, 1956). Vitrinite is most sensitive to weathering, while microcomponents of the inertinite and, particularly, exinite groups are more resistant to oxidation (Eremin, 1956; Manskaya and Drozdova, 1964; Butuzova et al., 1975; Eremin et al., 1980; Kucher et al., 1980; Sarbeeva, 1982). Some authors believe that oxidation of coals during the long-term storage under natural conditions does not lead to notable variations in the VR value (except for a slight decreasing trend), although some chemical parameters, such as the contents of carbon and oxygen, may vary significantly (Kukharenko, 1972; Stach et al., 1978; Marchioni, 1983; Stepanov, 1987). Other researchers demonstrated that the average VR value does not change at the initial stages of coal oxidation under natural conditions, because its chemical structure is not disturbed (Eremin, 1956; Sarbeeva, 1982; Eremin and Gagarin, 1999). At subsequent stages, the VR value decreases (Eremin, 1956). However, according to (Eremin and Gagarin, 1999), the VR value increases gradually due to rise in the degree of aromaticity with the removal of aliphatic components. Progressive oxidation of coals again provokes a new drop of VR values as a result of the formation of aromatic acids leading to decrease in aromaticity and condensation of nuclei in organic matter (Sarbeeva, 1982; Eremin and Gagarin, 1999). According to (Ammosov, 1967), the VR value increases at the initial stages of coal weathering and then decreases under conditions of strong oxidation down to values lower than in the unoxidized coal. Sabreeva (1982) recorded decrease of this parameter only for intensely metamorphosed coals, in particular, for semianthracites and anthracites. At the same time, some researchers (Alpern and Maume, 1969; Eremin et al., 1980) noted decrease in the VR parameter at the initial oxidation stage and its growth during the subsequent oxidation up to values exceeding those for the primary coal. Increase in the VR value in the course of oxidation of differently metamorphosed coals was reported in (Nandi et al., 1977).

One can also see similar contradictions in opinions concerning the influence of atmospheric oxygen on differently metamorphosed coals. Some authors (Babkin, 1972; Sarbeeva 1982) assumed that moderately metamorphosed coals are less resistant to oxidation. Sarbe-

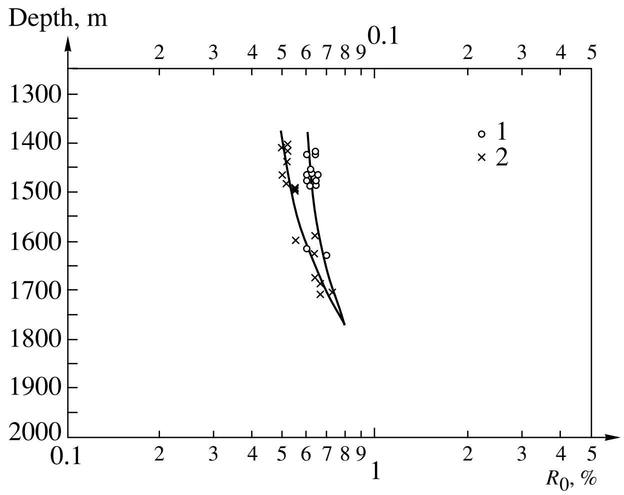

Fig. 1. Vitrinite reflectance (R_0, %) vs. depth plots for (1) primary and (2) oxidized Serpukhovian coals from Borehole 5-u.

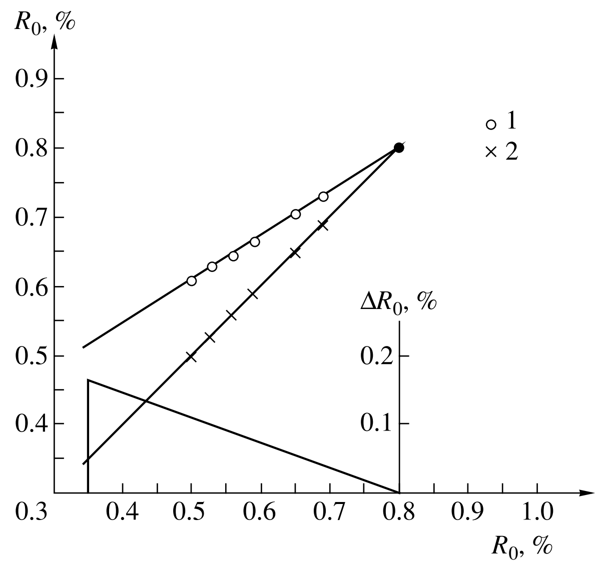

Fig. 2. Ratio between VR values (R_0, %) obtained for (1) primary and (2) oxidized coals.

eva attributed this phenomenon to elevated fissuring of their vitrinite. According to (Eremin, 1956; Kukharenko, 1972; Nandi et al., 1977; Reznik et al., 1980; Markova, 1990; Sallabasheva, 1992; and others), oxidation is most intense in slightly metamorphosed coals.

Contradictory opinions cited above indicate a baffling complexity of the oxidation process rather than insufficient knowledge of the problem. The oxidation process depends on many internal and external factors, such as the petrographic composition and fissuring of coals; type and dispersion degree of mineral admixtures; presence of metals with variable valence; degree of coal reduction; metamorphism grade, which determines the structural arrangement and chemical composition of organic matter; temperature regime and duration of oxidation; pH conditions; water content; and others.

We studied Lower Carboniferous coals from the Dobrudja foredeep located in the Dniester–Prut interfluve area between the ancient East European Platform and North Dobrudja fold zone. Our aim was to elucidate variations in the VR parameter in the course of the long-term storage of coals under atmospheric conditions.

The studied material was represented by coals and rocks with coal inclusions recovered from boreholes that penetrated the Lower Carboniferous (upper Visean–Serpukhovian) sequence in the Belyi Les block (eastern part of the Dobrudja foredeep) (Ivanova et al., 1998). Samples were taken by geologists from the Institute of Geological Sciences of the National Academy of Sciences of Ukraine in 1987 from cores stored outdoors for at least 5 yr.

The examined coals have largely humic composition. They contain all organic components. Vitrinite, the major component, is mainly represented by fibrous (less commonly, lumpy) attrite–vitrinite and desmite–vitrinite. Fusinized (attrite–fusinite and micrinite), lipoid (microexinite), and alginite (thallus- and colloalginite) microcomponents are subordinate. Mineral admixtures are represented by clayey material, pyrite, calcite, quartz, and feldspars.

In terms of microcomponent proportions, the coals are referred to the helitolite class and, less commonly, helitite types (*Petrograficheskie…*, 1975). The vitrinite, exinite, and inertinite contents (recalculated to organic matter) are 81–93, 3–14, and 2–12%, respectively. In helitites (with fusinized components) of the mixed lipoid–fusinite composition in some cases, the vitrinite, exinite, and inertinite contents are as high as 56–74, 3–24, and 16–25%, respectively.

The study of microscopic oxidation features in thin sections and polished sections revealed wedge-shaped and other microfissures related to weathering. Vitrinite demonstrates local leaching cavities. Some areas are characterized by the disintegration of vitrinite–desmite and the presence of the cellular structure. The lack of weathering rims with the lowered reflectance probably implies an intense oxidation of the organic matrix of coals. It is conceivable that the rims are just concealed, which is characteristic of slightly metamorphosed coals (Eremin, 1956; Alpern and Maume, 1969).

The VR values were measured in 1988 on polished sections and blocks in the air and immersion (cedar oil) medium using a POOS-1 device and monochromatic light (wavelength 546 nm). Optical glass materials TF2 and STF2 were used as standards.

Reflectance of vitrinite from Carboniferous sediments of the Belyi Les block

Ord. no.	Borehole no.	Sampling depth interval, m	Age	Study object	Reflectance	
					measured	corrected
1	3-u	1182–1186	C_1^{v2}	Vitrinized material in sandstone	0.71	0.74
2	"	1298–1304	C_1^{v1}	The same	0.90	0.90
3	4-u	1313–1317	C_1^{v2}	Durain in siltstone	0.39	0.54
4	"	1406–1409	"	Vitrinized material in sandstone	0.39	0.54
5	"	1555–1559	"	The same in argillite	0.43	0.56
6	"	1559–1563	"	The same in sandstone	0.45	0.58
7	"	1571–1576	"	The same	0.50	0.61
8	"	1649–1653	"	The same	0.59	0.67
9	"	1653–1657	"	The same in siltstone	0.59	0.67
10	"	1657–1661	"	The same in sandstone	0.57	0.65
11	5-u	1406–1411	C_1^{s}	The same in siltstone	0.53	0.62
12	"	1415–1418	"	The same in sandstone	0.50	0.61
13	"	1418–1422	"	The same	0.53	0.62
14	"	1443–1447	"	Clarain–durain in sandstone	0.53	0.62
15	"	1466–1471	"	Clarain–durain in sandstone	0.50	0.61
16	"	1483	"	Clarain in siltstone	0.51	0.61
17	"	1492–1495	"	Vitrinized material in sandstone and siltstone	0.55	0.64
18	"	1495–1499	"	the same in sandstone	0.55	0.64
19	"	1588–1592	"	The same	0.64	0.70
20	"	1596–1600	"	the same in argillite	0.55	0.64
21	"	1624–1628	"	clarain in sandstone	0.64	0.70
22	"	1672–1676	"	vitrinized material in sandstone and siltstone	0.64	0.70
23	"	1683–1687	"	clarain in argillite	0.67	0.72
24	"	1702–1706	"	clarain in argillite	0.73	0.76
25	"	1708–1712	"	vitrinized material in sandstone	0.67	0.72
26	6-u	1608–1612	C_1^{v2}	the same in argillite	0.65	0.70
27	"	1612–1616	"	the same in sandstone	0.65	0.70
28	"	1781–1785	"	The same	1.00	1.00

The VR values obtained for coals from Borehole 5-u appeared to be different from the values measured immediately after drilling and presented in the report of the Black Sea geological–prospecting expedition. Comparison of these data made it possible to compile a graph that exhibits the degree of VR variation in differently metamorphosed coals during their oxidation (Fig. 1). For the sake of clearness and convenience, the graph is transformed into the linear-dependence plot that demonstrates clearly the trend of decrease in the VR correction value (ΔR_o, %) toward the medium volatile bituminous coals (Fig. 2). This plot was used for correcting VR values obtained for samples from boreholes 3-u, 4-u, and 6-u, which recovered similar coals in Lower Carboniferous sediments of the Belyi Les block (Table). Based on the corrected data and in line with the method proposed in (Ivanova, 1992), we determined the catagenetic zoning in sedimentary rocks of the study region (Ivanova, 1995, 2002; Ivanova et al., 1998). It should be noted that the VR values averaged for each particular section are preliminarily taken for estimating the catagenetic transformation of rocks. The question as to whether or not these corrections can be extrapolated to Jurassic and Triassic coals recovered by boreholes 2-u (Nizhnii Prut salient) and 8-u (Dniester depression) remains to be solved.

The plot shows that variations in the VR value are particularly notable in the high volatile (B + C) bituminous coals (18–14%), less manifested in the high volatile A bituminous coals (11–6%), and are apparently lacking in the medium volatile bituminous coals.

Similar results were reported by the Bulgarian researchers (Markova, 1990; Sallabasheva, 1992) who studied Westphalian oxidized coals from the Dobrudja basin (L–P formations) that were stored indoors at room temperature for one year. In terms of the microcomponent composition, the examined coals belong to helitolites and mixtohumolites. The fusinite- and, less commonly, lipoid–fusinite–helitite types are defined among helitolites with the vitrinite, exinite, and inertinite contents (recalculated to organic matter) of 59–64, 6–17, and 21–31%, respectively. Mixtohumolites are represented by helite–fusinite–mixtohumitites with the vitrinite, exinite, and inertinite contents of 36–49, 16–23, and 35–49%, respectively. Sallabasheva (1992) established that the degree of coal oxidation shows negative correlation with the VR value, although the relationship is less notable than in our studies. This is probably explained by a shorter duration, favorable conditions of coal storage, and a different petrographic composition. Variations in minimal, medium, and maximal VR values are manifested with different intensities and at different intervals. Variations are most notable in the high volatile bituminous coals (7–8%). In medium and low volatile bituminous (fat and coking) coals, the variations are slow, irregular, and less distinct (2.6%). According to Markova (1990) who studied the influence of oxidation on the content of oxygen-bearing function groups, variations in the chemical composition are more significant for the high volatile bituminous coals and less notable for the medium volatile varieties as a result of structural features of coals.

The data obtained confirm the following notion: the higher grade of metamorphism, i.e., the higher content of aromatic nuclei and their condensation (coupled with simultaneous decrease in the number of side chains) leads to attenuation of the influence of oxidation on coals. In other words, highly metamorphosed coals are more resistant to oxidation. The degree of coalification shows negative correlation with the contents of carboxyl, carbonyl, and hydroxyl groups, peroxide compounds, bridge bonds, and other structures with unstable mobile oxygen atoms, resulting in high rates of coal oxidation by atmospheric oxygen (Titov and Khrisanfova, 1971). Under mild (atmospheric) conditions, the oxidant mainly interacts with the more reactive peripheral parts of coal structure to form humic acids and various lower-molecular oxidation products (Larina and Kasatochkin, 1960). The more ordered the coal surface structure, the more difficult the formation of surface oxides (Tarkovskaya, 1981). For example, oxygen is mainly amalgamated along the periphery of condensed nuclei in intensely metamorphosed coals. In slightly metamorphosed varieties, the amalgamation proceeds both along the periphery (with the rupture of side chains and aromatic rings) and between structural links of nuclei (Kukharenko, 1972).

The oxidation of coals leads to decrease in the condensation of aromatic nuclei and compactness of their arrangement. At the same time, the structure of oxidized coal becoming less ordered due to the higher share of aliphatic fragments. Therefore, decrease in the VR value of oxidized coal is quite natural.

The VR parameter is one of the main criteria for assessing the quality of coals and catagenetic transformations of host rocks. Data on the VR parameter make it possible to solve several issues of petroleum geology and to reconstruct the geothermal–geotectonic history of the region. Therefore, it is important to record and take into consideration variations in the VR parameter as a result of the oxidation of coals.

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