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AUTOXIDATION PROCESSES IN BITUMINOUS COAL FROM MINE 'KACHULKA', BALKAN BASIN (BULGARIA)

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Abstract. The study on the autoxidation processes occurring in the coal seam represents a definite interest in view of disturbing the ecological equilibrium. The object of investigation were bituminous coals from the Balkan coal basin, mine 'Kachulka', VI seam. Some analyses such as qualitative maceral, proximate, ultimate and functional analyses, have been applied. The oxidation level was evaluated after Grüner, Vesselovskii and the sum of acid groups (–OH and –COOH). Cluster analyses has been also performed. It has been proved that the oxidation level of the coals under study is similar to that of bituminous coals. The autoxidation processes in the seam from 'Kachulka' mine tend to increase their intensity from east to west. This observation is related to the higher content of clay minerals and pyrite. It has been also found that the inertinite macerals are products of the thermooxidation processes whose intensity has increased from west to east. These macerals have been found to be relatively resistant to the action of the atmospheric oxygen.

Keywords: autoxidation, bituminous coal, oxidation level, inertinite macerals.

AIMS AND BACKGROUND

The autoxidation processes occurring in the coal seam represent a particular interest. These processes lay in the basis of weathering, i.e. hypergenesis. The action of atmospheric oxygen under appropriate conditions might lead to coal self-ignition which has negative impact on the ecological system. From the other side, the changes in the coal composition, properties and structure lead to serious reduction of their technological characteristics and make them unsuitable as feed stocks. All this imposes the necessity of defining and characterising the areas in the coal seam most strongly affected by the autoxidation processes that have occurred in them. This problem has been studied more thoroughly for the bituminous and partially for the sub-bituminous coals[1-6].

The Balkan coal basin (60 km long) is located within the Balkan mountain, between the Shipka and Vratnik Passes. Its basement and surrounding rocks are of Paleozoic age – Triassic, Jurassic and Early Cretaceous. Kunchev et al.[7] distinguished three Formations in the cenomanian deposits, among which the second

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one is a coal-bearing formation composed of alternating, finely grained sandstones, clay sandstones, argillites and 2-3 to 8 coal seams (Fig. 1). The total thickness of the Formation ranges from 80 to 120 m and that of the coal seams – from 0.3 to 1.5 m. Kamenov et al.[8] reported some data on the lagoon environment and Nikolov[9] for the lagoon-bar environment. According to Petkov[10] the cenomanian geocomplex is paralimnic with two beds – limnic and paralic. The basin is a compex folded system and anticlines, synclines and thrusts have been recognised. The seams are nearly vertical in most of the coal deposits. The deposits are strongly faulted by a number of normal and strike-slip faults with amplitude up to 600-700 m. The coal is classified as bituminous of all classes.

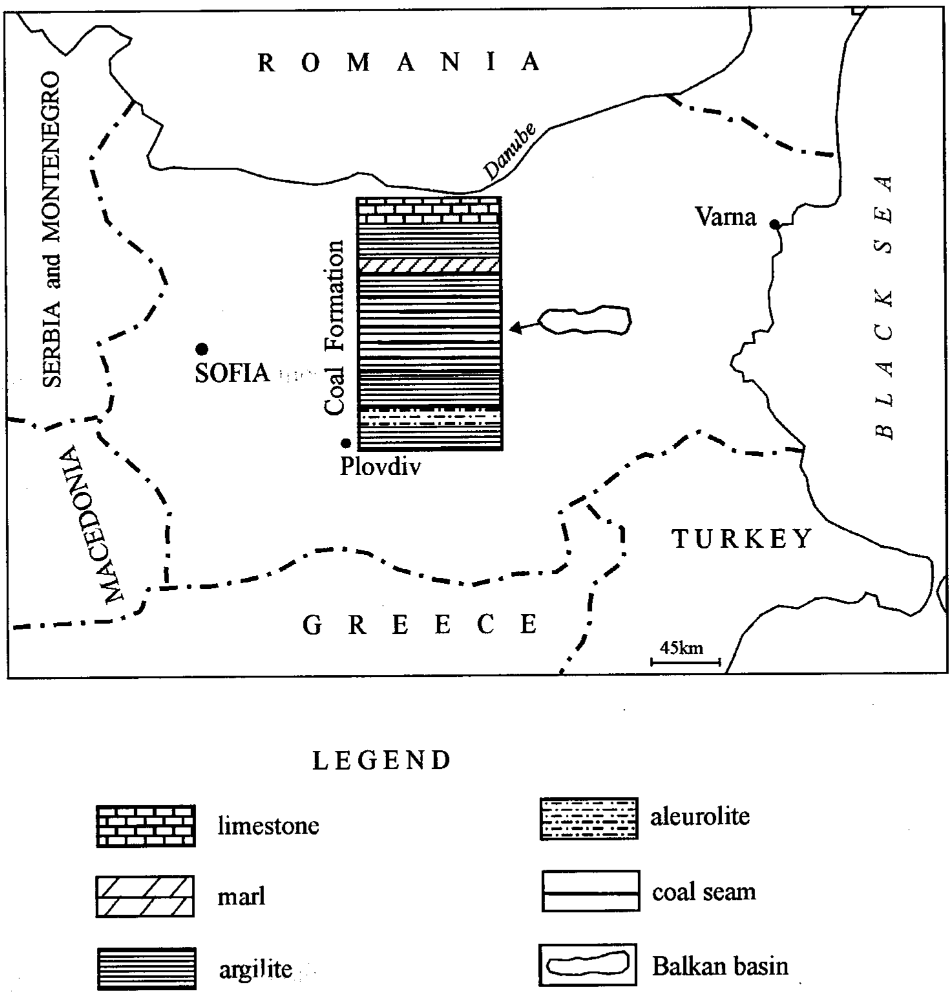

Fig. 1. Location of the Balkan coal basin and lithological column of the coal-bearing formation

The purpose of the present paper was to establish the distribution of macerals, minerals and oxygen-containing functional groups and the oxidation level of the coal from 'Kachulka' mine located in the eastern part of the Balkan basin, and to assess the autoxidation processes that have occurred in the coal seam.

EXPERIMENTAL

Bituminous coals, rank IV, indice C of the Balkan basin, mine 'Kachulka' – VI seam were studied. The sampling was carried out in 17 coal faces and 17 layer samples were taken (average of 51 layer-differential samples). Their distribution in the mine is demonstrated in Fig. 2. The quantitative maceral analysis was carried out on polished sections using an 'Amplival POL-U' microscope equipped with an Eltinor automatic point counter, in air atmosphere and oil immersion. The samples were subjected to ultimate, proximate and functional analyses. The proximate analysis (moisture, ash, and volatile matter yield) was performed after the corresponding Bulgarian standards. The ultimate analysis, particularly the determination of carbon and hydrogen content, was carried out on LECO-CHN 4000 and total sulphur was determined using LECO-CS-82 unit. Nitrogen content was determined by the Kjeldahl method. Organic sulphur was established by the difference between the total and the sum of sulphate and pyrite sulphur, the values of which were taken from literature data[11]. The oxygen amount was calculated by the difference to 100 %. The functional analysis included determination of oxygen-containing groups as follows: –OH (phenol) by treatment with barium hydroxide; carbonyl groups (>CO) – with hydroxylaminehydrochloride and carboxyl ones (–COOH) – by calcium acetate[12]. The oxidation level of the coals was evaluated using the method of Grüner[13], Vesselovskii[14] and after the sum of acid groups (–OH + –COOH) (Ref. 13).

A multiple statistical cluster analysis, P and Q modification, with correlation matrix of proximity was performed[15].

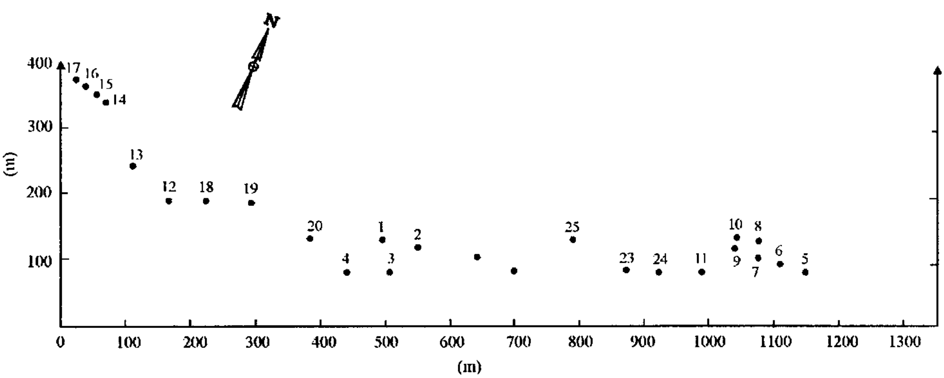

Fig. 2. Location of the coal samples from seam VI of mine 'Kachulka', Balkan coal basin (the numbers correspond to number of the samples used in the study)

RESULTS ANS DISCUSSION

According to the ICCP classification system for bituminous coal and anthracite[16], macerals of the three groups have been recognised in the coal under study.

Macerals of the Vitrinite group are dominant – their content varies from 30 to 80% (from 67 to 99% per organic matter) (Table 1). Collinite is the most abundant maceral – from 50% and up to 64% per organic matter. It is observed in the form of broad bands and big lenses and consists of the submacerals telocollinite and desmocollinite with the dominance of the first one. Tellinite is recognised as isolated lenses and is represented mainly by tellinite 2. Vitrodetrinite forms layers of various thickness, mainly in the highly ash areas of the coal seam.

Table 1. Maceral composition of bituminous coal from the VI seam of 'Kachulka' mine, Balkan coal basin (Bulgaria) (vol. %)

Sample No	Maceral composition (per total mass)						Maceral composition (per organic matter)		
	vitrinite, V	exinite, E	inertinite, I	clay minerals, Cl	pyrite, Py	other minerals	vitrinite, V	exinite, E	inertinite, I
5	78	8	1	8	3	2	90	9	1
6	79	6	1	10	4	–	92	7	1
7	79	6	2	10	2	1	91	7	2
8	70	2	12	10	6	–	83	3	14
9	72	2	1	15	9	1	96	3	1
10	78	5	4	8	4	1	90	6	4
11	30	1	5	50	8	–	86	2	12
2	71	4	3	12	8	2	91	5	4
3	72	7	6	10	5	–	85	8	7
1	72	9	7	8	4	–	82	10	8
4	68	5	4	11	12	–	89	6	5
12	79	5	3	10	3	–	91	6	3
13	69	7	9	10	4	1	81	8	11
14	79	1	–	10	10	–	99	1	–
15	75	4	1	10	7	3	94	5	1
16	80	4	9	5	2	–	86	4	10
17	31	11	4	35	18	1	67	24	9

The amount of the Exinite group macerals varies in broad ranges – from 1 to 11% (from 1 to 24% per organic matter) (Table 1). The macerals sporinite, cutinite, resinite and more rarely liptodetrinite have been also recognised. Sporinite is

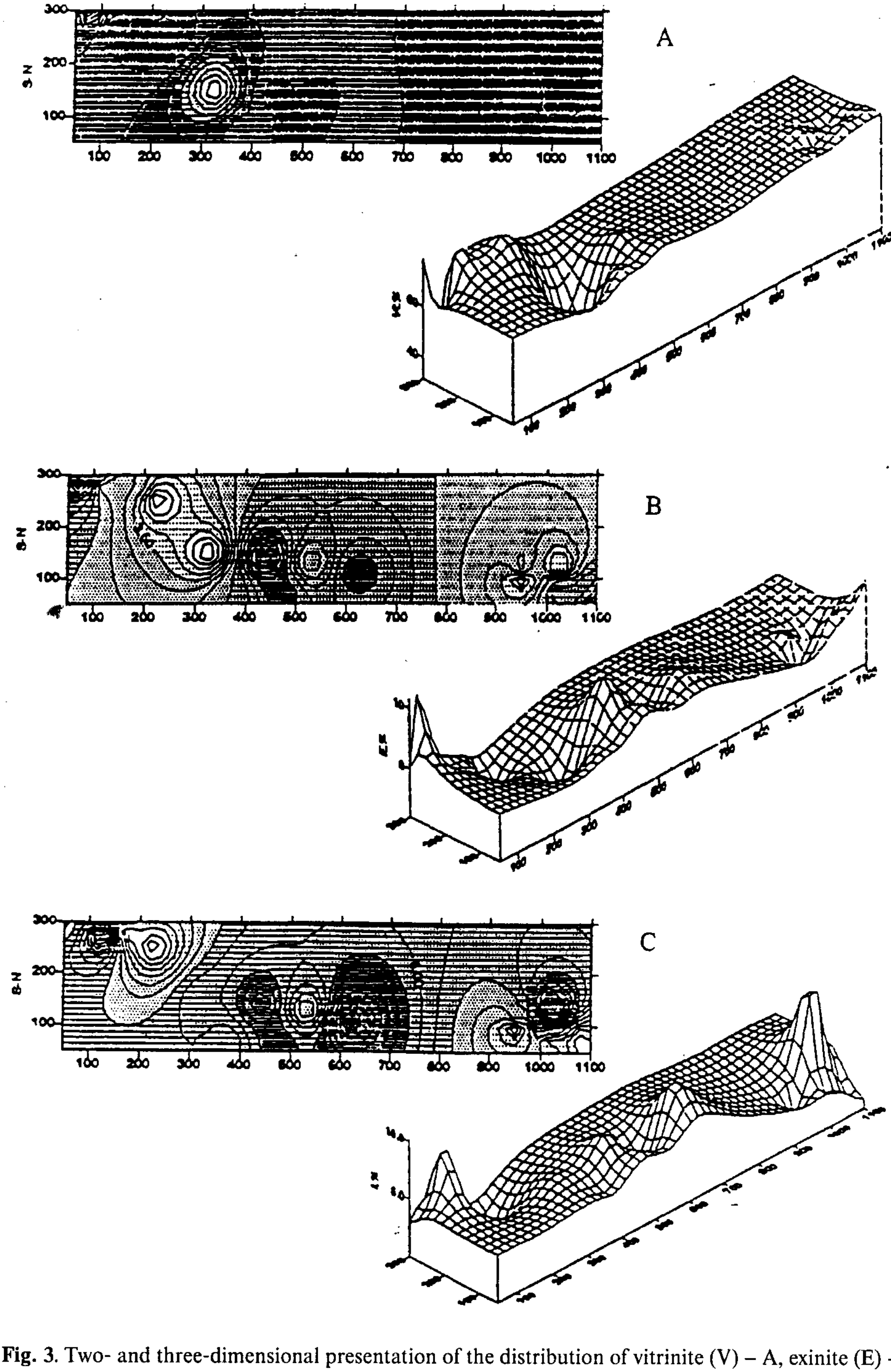

Fig. 3. Two- and three-dimensional presentation of the distribution of vitrinite (V) – A, exinite (E) – B, and inertinite (I) – C in seam VI of mine 'Kachulka', Balkan coal basin

represented mainly by miosporinite. Microsporinite, in associations most often with vitrodetrinite, is observed rarely. Isolated miospores have been observed in desmocollinite. Sporinite is only tenuisporinite. Cutinite, which is strongly crashed and associated with vitrodetrinite, contains mainly tenuicutinite. The amount of resinite is rarely over 2% and it is concentrated mainly in tellinite and collinite. Liptodetrinite is observed in vitrodetrinite, often in association with sporinite and cutinite. The content of the exinite macerals is maximum in samples Nos 17 and 16, i.e. 11 and 10%, respectively (Fig. 3).

The macerals of the Inertinite group are represented mainly by fusinite and semifusinite and to a smaller extent by sclerocinite and inertodetrinite. Most probably the conditions in the ancient peat bog had favoured the formation of fusainised macerals, particularly in isolated parts of the coal seam (Table 1). Fusinite is represented by its two varieties – piro- and degradofusinite. This maceral occurs as irregular grains with relatively well preserved cell structure. The amount of semifusinite is greater than that of fusinite. Piro- and degradosemifusinite are recognised as lenses, in association with collinite. Sclerocinite is mono-, two- and multichannel, while inertodetrinite associated with fusinite and semifusinite is observed as isolated small pieces. The content of inertinite macerals is higher in the following samples: No 8 – 14%, No 11 – 12%, No 13 – 11 % and No 16 – 10% (Table 1, Fig. 3).

Quartz, clay sulphide and carbonate minerals have been observed in the coal under study. The amount of quartz is higher in the eastern part of the studied area, in the vicinity of the coast line. It is present in the form of singular round grains of small dimensions. The clay minerals are represented mainly by illite and montmorilonite and to a smaller extent by kaolinite. Their percentage ranges from 5 to 50% (Table 1). These minerals associate predominantly with vitrodetrinite, more randomly with tellinite, fusinite and semifusinite. They also occur together with vitrodetrinite forming layers in the coal seam. Sample No 17 contains a high percentage of clay minerals and pyrite, too. Particularly high is the content of these minerals in sample No 11 – 50 % (Table 1, Fig. 4, B). Sulphide minerals occur as pyrite and to a smaller extent as marcasite, halcopyrite and galenite. The high content of pyrite, varying from 2 to 18% (Table 1), might be related to the sea transgression. The framboidal pyrite is poorly presented. Massive, anhedral and euhedral pyrite have not been observed. Epigenetic infiltration pyrite is deposited in the cracks of the coal seam. Pyrite often associates with vitrodetrinite and clay minerals.

Carbonate minerals are present as calcite, dolomite, siderite and randomly as ancerite and magnesite. Epigenetic carbonates filling the caolinite cracks and cleavages are dominant.

The results of the technical analysis show that the analytical moisture in the coal from the 'Kachulka' mine varies from 0.3 to 1.0% (average 0.5%). The varia-

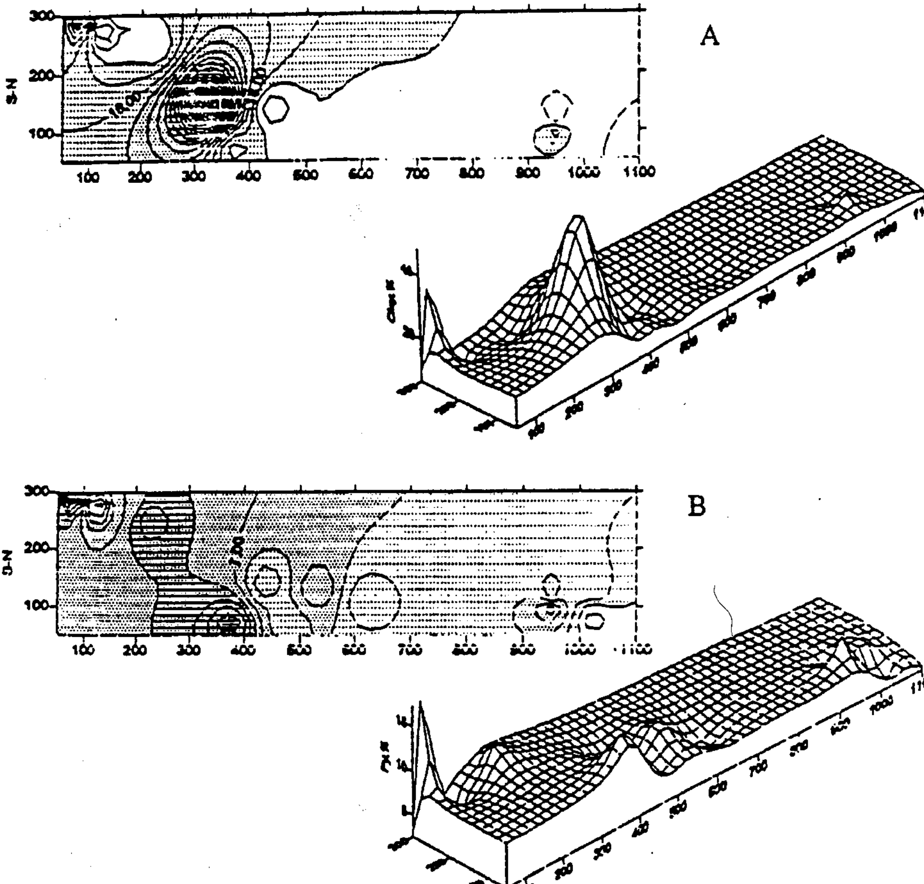

Fig. 4. Two- and three-dimensional presentation of the distribution of clay minerals (Cl) – A, and pyrite (Py) – B in seam VI of mine 'Kachulka', Balkan coal basin

tions in the ash content are from 19.1 to 55.0% (average 37.6%). Because of the high ash content of the coal under study, the yield of volatile matter was not determined. This was possible only in the case of two samples, i.e. No 2 – 38.1.8% and No 14 – 28.5% (Table 2).

The content of carbon is within the limits of 81.5 and 88.8%, of hydrogen – 3.4 to 4.6%, of nitrogen – 1.0 to 1.4%, of organic sulphur – from 0.4 to 3.9% and of oxygen – from 4.6 to 9.9% (Table 2).

The content of hydroxyl groups is varying from 0.71 to 1.1 meq/g (average 0.84 meq/g), of carbonyl – 0.14 to 0.90 meq/g (average 0.33 meq/g) and of carboxyl – from 0.03 to 0.10 meq/g (average 0.05 meq/g)(Table 3). The amount of –OH groups is maximum for samples Nos 5, 13, 14 and 17, of >CO – for Nos 5,

Table 2. Characteristics of bituminous coal samples from the VI seam of mine 'Kachulka', Balkan coal basin (Bulgaria)

Sample No	Proximate analysis (wt. %)			Ultimate analysis (wt. %)					Atomic ratios	
	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	N^{daf}	S_{org}	O^{daf}	H/C	O/C
5	0.3	38.3	–	87.5	3.6	1.3	0.9	6.7	0.49	0.06
6	0.4	45.2	–	88.3	4.1	1.1	1.2	5.3	0.56	0.05
7	0.5	35.5	–	87.4	4.1	1.1	0.4	7.0	0.56	0.06
8	0.5	48.0	–	88.8	4.3	1.2	1.1	4.6	0.58	0.04
9	0.7	55.0	–	88.7	4.1	1.4	1.1	4.7	0.56	0.04
10	0.6	34.8	–	87.2	4.6	1.4	0.7	6.1	0.63	0.05
11	0.8	54.9	–	85.5	3.5	1.1	0.4	9.5	0.49	0.08
2	0.4	23.6	38.1	87.0	3.8	1.3	1.0	6.9	0.53	0.04
3	0.4	40.7	–	86.0	4.3	1.3	0.6	7.8	0.60	0.07
1	0.5	30.8	–	86.4	4.0	1.4	2.0	6.2	0.56	0.05
4	0.3	30.8	–	86.5	3.9	1.3	1.8	6.5	0.54	0.06
12	0.5	44.8	–	85.9	4.1	1.3	0.6	8.1	0.57	0.07
13	0.5	35.6	–	86.0	3.5	1.3	2.7	6.5	0.49	0.06
14	0.6	19.1	28.5	85.8	3.4	1.4	3.5	5.9	0.48	0.05
15	0.3	41.4	–	86.2	4.0	1.2	1.7	6.2	0.56	0.05
16	1.0	29.1	–	86.4	3.9	1.3	1.6	6.8	0.54	0.06
17	0.8	31.9	–	81.5	3.7	1.0	3.9	9.9	0.54	0.09

15 and 17 and for –COOH – Nos 9, 14 and 17 (Table 3, Fig. 5). The sum of oxygen-containing functional groups is within the range 1.00-2.07 meq/g (average 1.12 meq/g). The content of functional oxygen varies from 1.65 to 3.42% (average 2.1%), and that of non-functional from 2.7 to 7.3% (average 4.5%). The content of functional oxygen increases from east to the west whilst that of non-functional oxygen is maximum for the coals from the middle parts of the coal mine under study (Table 3).

The oxidation level after Grüner varies from 1.4 to 3.0 (average 2.1), after Vesselovskii from –0.0681 to –0.1230 (average –0.0949) and after the sum of –OH and –COOH from 0.76 to 1.17 meq/g (average 0.93 meq/g) (Table 3). The values of this index are relatively higher for samples Nos 5, 11, 14 and 17 (Fig. 6).

Two complexes A and B (Fig. 7) are distinguished on the dendrogram of the coal from mine 'Kachulka'. Complex A consists of one group including the indi-

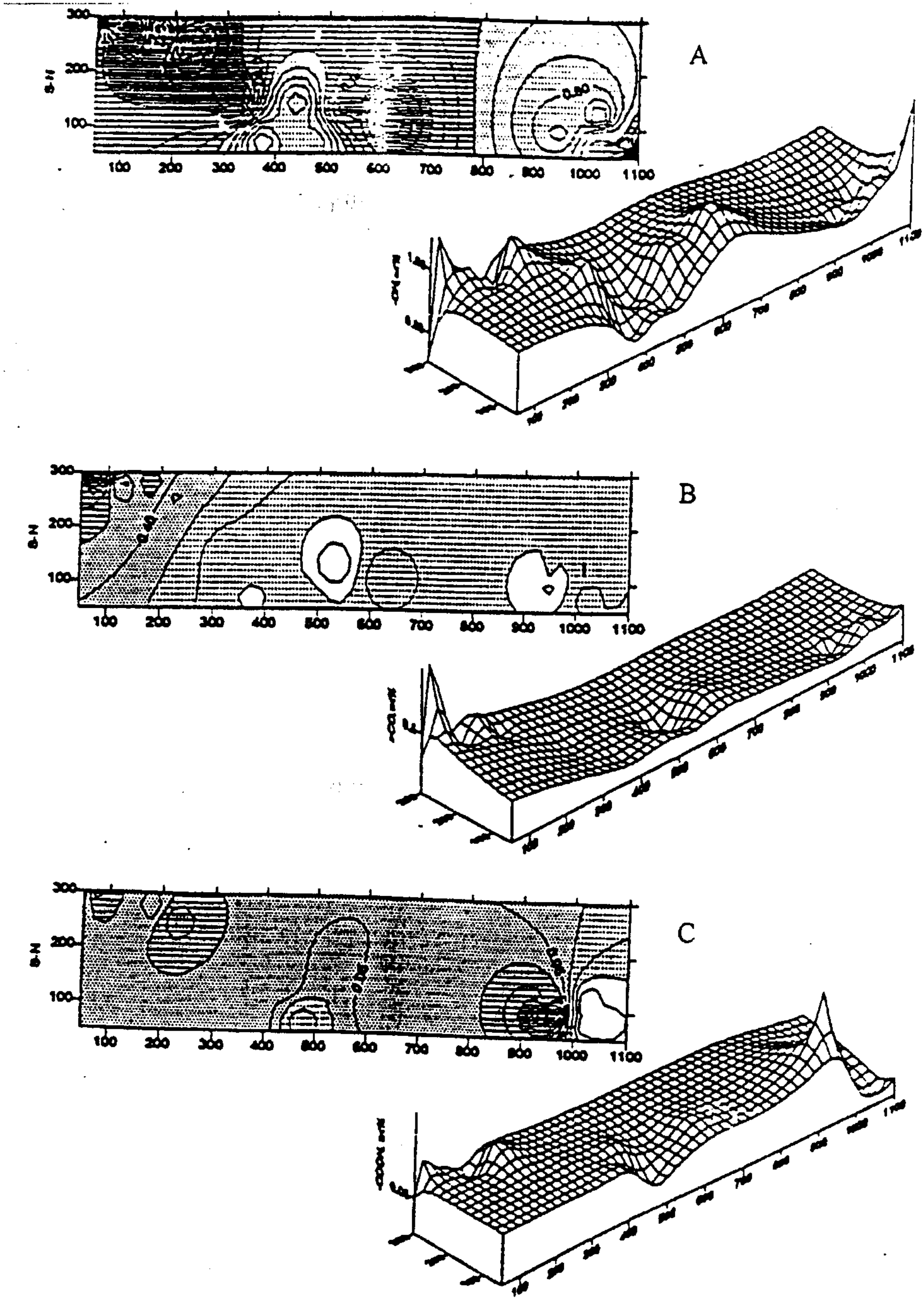

Fig. 5. Two- and three-dimensional presentation of the distribution of oxygen-containing functional groups: hydroxyl (–OH) – A, carbonyl (>CO) – B, and carboxyl (–COOH) – C in seam VI of mine 'Kachulka', Balkan coal basin

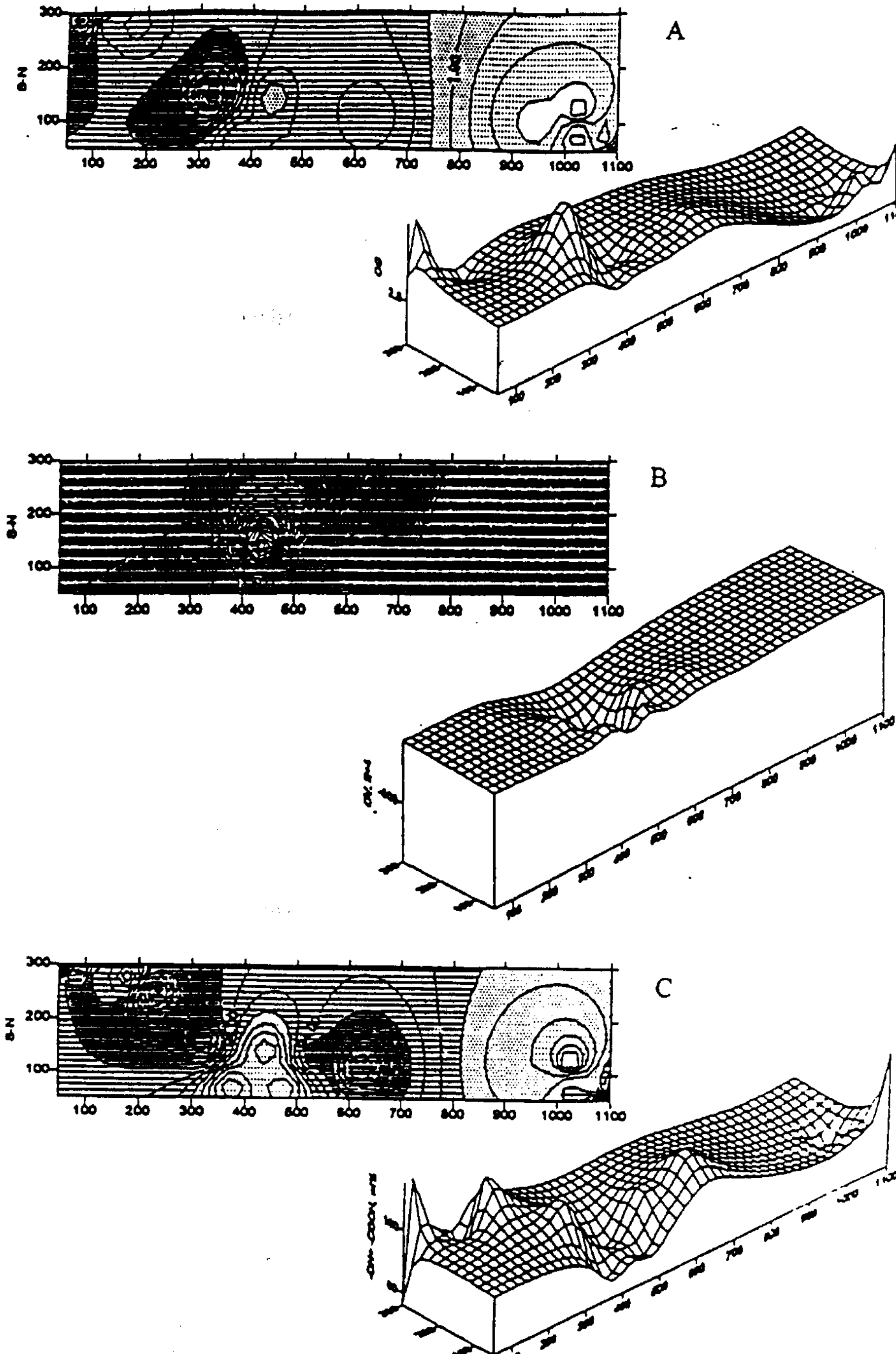

Fig. 6. Two- and three-dimensional presentation of the distribution of oxidation level after Grüner (A), after Vesselovskii (B) and after the sum of oxygen-containing acid functional groups (–OH + –COOH, meq/g) (C) in the VI seam of mine 'Kachulka', Balkan coal basin

Table 3. Oxygen-containing functional groups and oxidation level of bituminous coals from the VI seam of 'Kachulka' mine, Balkan coal basin , Bulgaria

Sample	Oxygen-containing functional groups									Oxidation level after:		
No	–OH (meq/g)	>CO (meq/g)	–COOH (meq/g)	sum (meq/g)	–OH (%)	>CO (%)	–COOH (%)	O_f (%)	O_{nf} (%)	Grüner	Vesse-lovskii	–OH + –COOH (meq/g)
5	1.10	0.36	0.04	1.50	1.76	0.58	0.13	2.47	2.7	2.3	–0.0853	1.14
6	0.84	0.28	0.03	1.15	1.34	0.45	0.10	1.89	3.4	1.6	–0.1070	0.87
7	0.88	0.34	0.03	1.25	1.41	0.54	0.10	2.05	5.0	2.0	–0.1042	0.91
8	0.73	0.24	0.03	1.00	1.17	0.38	0.10	1.65	3.0	1.4	–0.1161	0.76
9	0.76	0.18	0.10	1.04	1.22	0.29	0.32	1.83	2.9	1.5	–0.1082	0.86
10	0.80	0.26	0.06	1.12	1.28	0.42	0.19	1.70	4.4	1.6	–0.1230	0.86
11	0.98	0.27	0.06	1.31	1.57	0.43	0.19	2.19	7.3	3.0	–0.0746	1.04
2	0.93	0.14	0.05	1.12	1.49	0.22	0.16	1.87	5.0	2.2	–0.0914	0.98
3	0.78	0.28	0.04	1.10	1.25	0.45	0.13	1.83	6.0	2.1	–0.1076	0.82
1	0.76	0.26	0.06	1.08	1.22	0.42	0.19	1.83	4.4	1.9	–0.0973	0.82
4	0.74	0.24	0.06	1.04	1.18	0.38	0.19	1.75	4.7	2.0	–0.0936	0.80
12	0.71	0.35	0.05	1.11	1.14	0.56	0.16	1.86	6.2	2.3	–0.0995	0.76
13	1.00	0.34	0.06	1.40	1.60	0.54	0.19	2.33	4.2	2.2	–0.0763	1.06
14	1.04	0.34	0.07	1.45	1.66	0.54	0.22	2.42	3.5	2.2	–0.0717	1.11
15	0.83	0.49	0.05	1.37	1.33	0.78	0.16	2.27	4.6	2.1	–0.0966	0.88
16	0.89	0.32	0.06	1.27	1.42	0.51	0.19	2.22	4.7	2.1	–0.0933	0.95
17	1.10	0.90	0.07	2.07	1.76	1.44	0.22	3.42	4.5	3.0	–0.0681	1.17

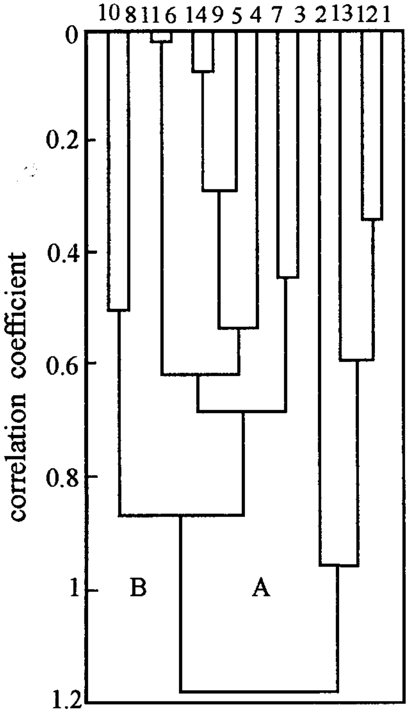

Fig. 7. Dendrogram from the cluster analysis of coal from mine 'Kachulka', Balkan coal basin
1 – vitrinite, V (%); 2 – exinite, E (%); 3 – inertinite, I (%); 4 – pyrite, Py (%); 5 – clay minerals, Cl (%); 6 – hydroxyl groups, –OH (meq/g); 7 – carbonyl groups, >CO (meq/g); 8 – carboxyl groups, –COOH (meq/g); 9 – oxidation level after Grüner – OLG; 10 – analytical moisture – W^a (%); 11 – oxidation level after the sum of acid groups, –OH + –COOH (meq/g); 12 – carbon, C^{daf} (%); 13 – hydrogen, H^{daf} (%); 14 – oxygen content, O^{daf} (%)

ces: content of vitrinite and carbon from the one side, and from the other, the content of hydrogen as well as exinite as an independent index. The correlation between the content of vitrinite and carbon is particularly significant (Fig. 7, Table 4). The correlation of exinite with the other parameters is weak and insignificant.

The second complex B is composed of two groups (Fig. 7, Table 4). The first group is subdivided into two sub-groups. The first sub-group includes the content of inertinite and carbonyl groups with a strong and significant correlation. The second sub-group is split into two: the first one combines the content of pyrite, clay minerals and oxygen and oxidation level after Grüner, and the second one – the quantity of hydroxyl groups and the sum of acid groups (–OH + –COOH). The correlations between the first four parameters and between the last two are strong and significant. The second group of complex B includes the amount of carboxyl groups and the content of analytical moisture with a strong and significant dependence.

Table 4. Correlation matrix of the base indices for bituminous coals from 'Kachulka' mine, Balkan coal basin, Bulgaria*

Index	V	E	I	Py	Cl	–OH	>CO	–COOH	OLG	W^a	–OH + –COOH	C^{daf}	H^{daf}	O^{daf}
V	1.00	–0.14	–0.12	–0.66	–0.95	–0.36	–0.49	–0.27	–0.73	–0.11	–0.41	0.66	0.38	–0.71
E	–0.14	1.00	0.05	–0.18	–0.03	–0.15	–0.10	–0.16	–0.06	0.29	–0.23	–0.00	0.15	–0.02
I	–0.12	0.05	1.00	0.05	–0.09	0.20	0.55	–0.18	0.23	–0.18	0.19	–0.46	0.03	0.35
Py	–0.66	–0.18	0.05	1.00	0.55	0.24	0.52	0.49	0.42	0.16	0.35	–0.60	–0.33	0.33
Cl	–0.95	0.03	–0.09	0.55	1.00	0.35	0.36	0.26	0.72	0.44	0.41	–0.53	–0.40	0.69
–OH	–0.36	–0.15	0.20	0.24	0.35	1.00	0.49	0.11	0.64	0.32	0.98	–0.49	–0.76	0.42
>CO	–0.49	–0.10	0.55	0.52	0.36	0.49	1.00	0.09	0.56	0.23	0.50	–0.81	–0.25	0.56
–COOH	–0.27	–0.16	–0.18	0.49	0.26	0.11	0.09	1.00	0.15	0.49	0.13	–0.26	–0.26	0.03
OLG**	–0.73	–0.06	0.23	0.42	0.72	0.64	0.56	0.15	1.00	0.32	0.66	–0.83	–0.68	0.92
W^a	–0.41	0.29	–0.18	0.16	0.44	0.32	0.23	0.49	0.23	1.00	0.28	–0.34	–0.15	0.32
–OH + –COOH	–0.42	–0.23	0.19	–0.35	0.41	0.98	0.50	0.23	0.66	0.28	1.10	–0.52	–0.79	0.42
C^{daf}	0.66	–0.00	–0.46	–0.60	–0.53	–0.49	–0.81	–0.26	–0.83	–0.34	–0.52	1.00	0.42	–0.82
H^{daf}	0.38	0.15	0.03	–0.33	–0.40	–0.76	–0.25	–0.26	–0.68	–0.15	–0.79	0.42	1.00	–0.35
O^{daf}	–0.71	–0.02	0.35	0.33	0.69	0.42	0.56	0.03	0.92	0.32	0.42	–0.82	–0.35	1.00

*The correlations are significant at $p<0.05$; number of samples studied – 17; $r_0 = 0.49$; minimum statistical significant value; **OLG – oxidation level after Grüner.

Thus, the results of the cluster analysis point to a strong and significant positive correlation between the oxidation level after Grüner and the content of oxygen-functional groups, particularly of –OH and –COOH, clay minerals and total oxygen content. The dependencies between pyrite and carbonyl and carboxyl groups, between inertinite and carbonyl groups and between analytical moisture and carbonyl groups are relatively stronger and more significant.

The coal from the VI seam of 'Kachulka' mine, Balkan coal basin, has an oxidation level as follows: 2.1 after Grüner and –0.0949 after Vesselovskii, which corresponds to that for bituminous coal[14]. An increase in this parameter from east to west in the mine (Fig. 6, A, B, C) has been observed. The change in the content of oxygen-containing functional groups (–OH, >CO and –COOH) follows a similar tendency (Fig. 5, A, B, C). The increase in pyrite and clay minerals content follows the same direction (Fig. 4, A, B). The same refers for inertinite and exinite macerals (Fig. 3, A, B). The content of inertinite decreases (Fig. 3, C). The autoxidation processes in this case are strongly influenced by the quantity of oxygen-containing functional groups, pyrite, clay minerals and the oxidation level, whose strong correlation is proved by the cluster analysis (Table 4, Fig. 7). This conclusion is in accordance with the deductions made for other coal types (Refs 4-6 and 17-19). Thus, the organic coal matter rich in clay substances and pyrite is oxidised more intensively. Due to their weak thermal conductivity, these ingredients contribute to accumulation of the heat released from the oxidation processes occurring in the neibouring layers[6,20]. The results also indicate that the intensity of the autoxidation process in the coal of 'Kachulka' mine increases from east to west direction.

The area distribution of the inertinite macerals (Fig. 3,C), respectively of the increase in their content from west to east, contrary to the changes established for some parameters (the quantity of oxygen functional groups and oxidation level) points to the higher oxidative stability of inertinite macerals (Refs 4-6 and 17-19). The higher content of these macerals in the eastern part of the mine, together with the lower content of oxygen-containing functional groups and the lower values of the oxidation level are in support of the assumption for their generation in the course of intensified thermooxidation processes.

CONCLUSIONS

1. The oxidation level of the coal from the VI seam of 'Kachulka' mine, Balkan coal basin, is similar to that for bituminous coal.

2. The intensity of the autoxidation processes in the investigated mine increases from east to west, most probably as a consequence of the enhanced content of clay minerals and pyrite.

3. Inertinite macerals have been generated at thermooxidation processes with increasing intensity from west to east.

4. The inertinite macerals are relatively stable to the action of atmospheric oxygen.

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