ELECTRONIC STRUCTURE AND BIOLOGICAL ACTIVITY OF NATIVE COALS

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Abstract

Disabilities of coal miners due to black-lung decease morbidities are rather high (up to 10 men per 1 million tons of mined coal). Besides that, dangerous to health biological activity is also proper to various carbon nanoparticles. The analysis of relationships between coal miner morbidities, biological activities of coals and bibliographical data has shown that: activity of coals is mainly determined by their organic matter but not their silica admixtures in mineral matter of coals; among the different types of coals, an increased activity is proper to anthracites and among the different petrographical components of coals an increased activity is proper to fusainite; activity of oxidized coals is considerably lower than that of non-oxidized ones; action of ozone and coal and silica particles on fagocytes is essentially similar; oxygen can be reduced on both coal and silica surfaces to biologically dangerous ion-radical species, followed by generation (in the presence of water) of highly active $OH^{\bullet}$-radicals; effect of coal particles on lungs is related to violation of coal particles removal from lungs as a result of transportation cells (fagocytes) destruction and coal accumulation in the interalveolar lung spaces.

Characteristics of electron interactable with oxygen can be estimated from ESR spectra of unpaired electrons (UE) in non-oxidized coal placed under methane atmosphere. The parameter of coal ability to reduce oxygen is proportional to the concentration of UEs interactable with O_2 and is reciprocally proportional to the ESR line width of non-oxidized -native coal UEs before air exposition. The parameter of biological activity (coal ability to violate biological membranes), K_{Φ}, is proportional to logarithm of the parameter of coal electron-donor ability. The parameter K_{Φ} was estimated for coal samplesFig.2 (of various coal ranks ranging from jet coal to anthracite) selected from 44 coal beds in the 11 coal mines of Kuzbass (Russia). The K_{Φ} values obtained were compared with morbidity parameters (relative amounts of disabled coal miners per 1 million of mined coal). It has been established that the incidence of disease, P, is linearly (with correlation coefficient of 0.95) related to K_{Φ} values determining the ability of coal dust to reduce oxygen and to accelerate the destructive oxidation of biological membrane lipids. At the same time, the numerical K_{Φ} and P values are equal.

Thus, the mechanism of an initiating role of coal electrons interactable with oxygen to form biologically active pathogenic species has been established. A method for estimation of coal fibrinogen activity, comprising the determination of the amounts and mobilities of unpaired electrons (from the ESR measurements) reducing oxygen into biopathogenic species has been developed. A considerable increase in biopathogenic activity for non-oxidized coal dust particles compared to that of oxidized coal has been discovered. A complex of methods for the selection, pretreatment and studying of native coals, permitting one to investigate their biopathogenic properties.

Keywords bioactivity, native coal, electronic structure, ESR.

Introduction.

Disabilities of coal miners due to black-lung decease morbidities are rather high (up to 10 men per 1 million tons of mined coal). Besides that, dangerous to health biological activity is also proper to various carbon nanoparticles. For planning security measures in the course of coal mining it is necessary to elucidate the mechanism of coal action on biological membranes of pulmonary fagocytes providing the purification of air-cells[*], to find out a carbon matrix property determining this biological activity and to develop the method for quantitative estimation of this property. The analysis of relationships between coal miner morbidities, biological activities of coals and bibliographical data has shown that:

- activity of coals is mainly determined by their organic matter but not their silica admixtures in mineral matter of coals;
- among the different types of coals, an increased activity is proper to anthracites and among the different petrographical components of coals an increased activity is proper to fusainite;

[*] These fagocytes are violated under the action of active particles of coal dust.

- activity of oxidized coals is considerably lower than that of non-oxidized ones;
- action of ozone and coal and silica particles on fagocytes is essentially similar;
- oxygen can be reduced on both coal and silica surfaces to biologically dangerous ion-radical species, followed by generation (in the presence of water) of highly active $OH^{\bullet}$-radicals;
- effect of coal particles on lungs is related to violation of coal particles removal from lungs as a result of transportation cells (fagocytes) destruction and coal accumulation in the interalveolar lung spaces.

Thus, the key property determining biological activity of coal may be related to its ability to convert (reduce) oxygen into ion-radical species. It is known that apparent activation energies of the oxidation process decrease with coal rank increases in spite of diminishing of easily oxidizable aliphatic fraction in the organic matter of coal. At the same time, the oxidation activation energies and numerical values of electroconductivity activation energy for highly-metamorphized coals are coincident (about 10 kcal/mol). Hence, it is necessary:

- to develop the method for estimation of the property determining oxygen reduction rates on coals;
- to develop methods for the selection, pretreatment and studying of coal materials similar to non-oxidized native coals in coalbeds of coal mines;
- to estimate biological activity in model experiments.

As it follows from the analysis of electrochemical redox process equations on the surfaces of semiconductors, the factors determining the rate of electrochemical reaction are the concentration of conductivity electrons (n_s) and electron energy at the bottom of conduction band (E_{Cs}). The rate of oxygen reduction process is proportional to

$$n_s \infty \exp[-\frac{(E_{Cs} - E_o)^2}{4\lambda kT} \qquad (1)$$

where E_o is electron energy at vacant level of oxygen molecule in solution;

λ is rearrangement energy of polar medium;

k is a Bolzmann constant;

T is temperature (K).

The charge transfer in the organic semiconductors with polyconjugated π-electron systems does not occur via the band mechanism but through the electron jump mechanism. Therefore, the reduced oxygen molecules can leave an electron-donating domain of conjugated systems only after the adjacent domain electron can recombine with the hole formed. Hence, the electron-donor ability in the reduction process of oxygen is determined by the concentration of electrons capable to diffuse through carbon matrix and their mobility related to the conductivity activation energy and electron work function.

Indeed, with coal rank increasing, the concentration of conductivity electrons tends to rise but conductivity activation energy tends to fall. During the coal oxidation a reverse process takes place. The conductivity of fusain is several orders higher than that of other petrographical coal components. Thus, the main parameters determining oxygen reduction rate on coal surface are the concentration of electrons interactable with oxygen and their mobility in carbon matrix. These parameters can be estimated by the electron spin resonance technique (ESR). Relaxation time of unpaired electrons, T_1 (sec), is related to their ESR line width by the equation:

$$T_1 = \frac{3 \cdot 10^{-5}}{4\pi \cdot \Delta H} = \frac{1}{30} \frac{\tau_p}{(g - g_e)^2} \qquad (2)$$

where g and g_e are g-factor of unpaired electron in the coal sample studied and

g-factor of free electron, respectively;

ΔH is semi-width of the ESR line for coal unpaired electron (A/M);

τ_p is relaxation time of unpaired electron as charge carrier (sec).

Thus, characteristics of electron interactable with oxygen can be estimated from ESR spectra of unpaired electrons (UE) in non-oxidized coal placed under methane atmosphere (i.e. under coalbed medium) (Fig.1).

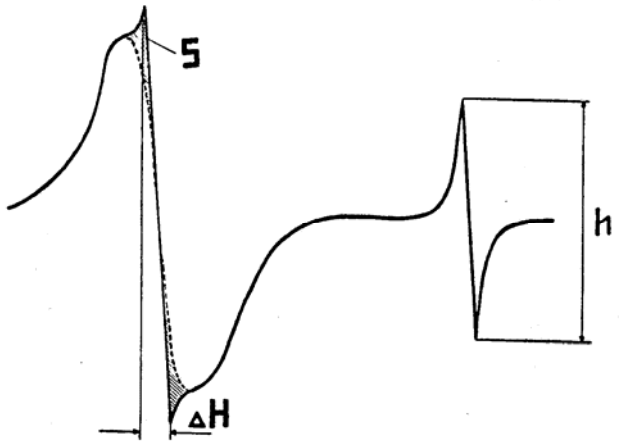

Fig.1.ESR-spectra of samples the native coal containing methane: S - the unpaired electron line area, and •H is its width, h – Mn^{2+} 4th line amplitude as a standard.

Changes in UE concentration during coal interaction with air is determined by the concentration of UEs belonging to oxygen. From the ESR line sensible to the interaction studied the value proportional to the mobility of UEs interacting with O_2 can be found. The concentration of coal UEs interactable with O_2 (N_b) is evaluated as product of change in the ESR line amplitude during methane substitution in coal by air (for 30 s) and concentration of UEs in non-oxidized coal under methane atmosphere(Berveno, 1998). Since the mobility of UEs in carbon matrix is reciprocally proportional to the ESR line width of UEs interactable with oxygen, the parameter of electron-donating ability, R, can be written as:

$$R \propto \left(\frac{N_b}{\Delta H} \right) \tag{3}$$

For convenience, a relative R values were used in comparison with R_{min}, the value of the least active coal sample. Thus, the parameter of coal ability to reduce oxygen is proportional to the concentration of UEs interactable with O_2 and is reciprocally proportional to the ESR line width of non-oxidized -native coal UEs before air exposition.

But the oxidation rate of oxygen-activated biological membranes, as well as the radical-chain process, are not determined only by chain initiations but also chain ruptures. Activated oxygen involves in both processes. In one of the similar processes, lipid oxidation, the rate is proportional to logarithm of active iron ions (Fe^{2+}) concentration. The same dependence is also proper to cumene oxidation in the presence of active carbon: oxidation rate is proportional to logarithm of coal concentration, i.e., concentration of active sites interacting with cumene. Thus, it should be expected that the parameter of biological activity (coal ability to violate biological membranes), K_{Φ}, is proportional to logarithm of the parameter of coal electron-donor ability, R:

$$K_{\Phi} = \ln R_{rel} = \ln N_{surf} / (R_{\min} \cdot \Delta H) \tag{4}$$

The parameter K_Φ was estimated for coal samplesFig.2 (of various coal ranks ranging from jet coal to anthracite) selected from 44 coal beds in the 11 coal mines of Kuzbass (Russia).

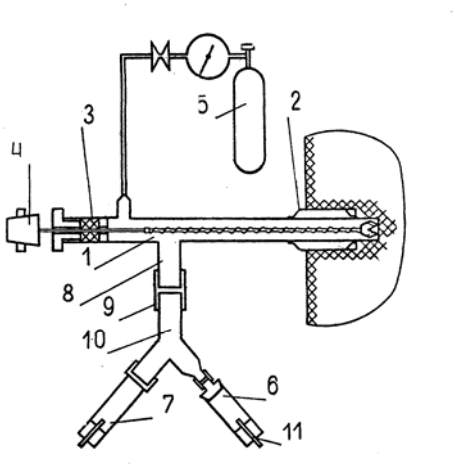

Fig. 2. Scheme of coal sampling: 1 – housing; 2 – capsulator; 3 – packing gland; 4 – drill rod with shank; 5 – methane cylinder; 6,7 – culm receivers; 8 – nipple for coal taking; 9 – connecting hose; 10 – T-joint; 11- connecting pipe for air fault.

The K_Φ values obtained were compared with morbidity parameters (relative amounts of disabled coal miners per 1 million of mined coal) (see Fig.3). It has been established that the incidence of disease, P, is linearly (with correlation coefficient of 0.95) related to K_Φ values determining the ability of coal dust to reduce oxygen and to accelerate the destructive oxidation of biological membrane lipids (Fig.4). At the same time, the numerical K_Φ and P

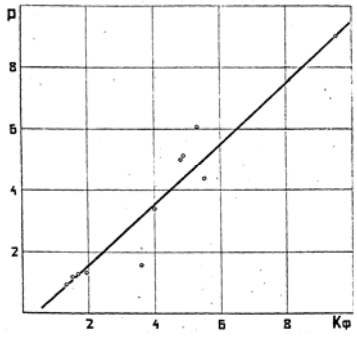

Fig. 3. The relationship between predictable coal dust fibrinogenic activity coefficient (K_Φ) and black-lung decease morbidity of coal miners (P).

values are equal. The relationship between R and P values is less pronounced, compared to that between K_Φ and P. This can be considered as an indicative of participation of active oxygen in both the chain initiation and rupture of radical oxidation of lipids.

Besides that, this parameter was compared with biologically measured:

- time of red cell hemolysis under the coal dust action (coal cytopathogenicity);
- phagocytal number (amount of coal dust particles trapped by alveolar phagocytes and neutrophils.

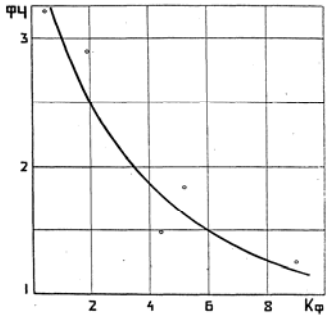

Fig. 3. Influence of predictable coal dust fibrinogenic activity coefficient ($K_Ф$) on the coal dust trapping activity of phagocytes (phagocytal number).

In the biological experiments, the effects non-oxidized and oxidized coal dust particles (of < 5 mcm in size) on the alveolar phagocytes of white mice and human red cells and neutrophils have been investigated. It has been found that the effect of the oxidized anthracite dust on neutrophils is practically identical to the action of the non-oxidized middle-rank coal dust (30 ± 1.7 and 32 ± 1.0, respectively) (Table 1).

Table 1

Effect of oxidation degree and various coal rank dusts on red cells

Dust oxidation degree	Time of hemolysis under thecoal dust action (min)		
	Jet coal ($K_Ф$ = 1.22)	Low-caking coal ($K_Ф$ =6.02)	Anthracite ($K_Ф$ = 9.21)
Non-oxidized	50+/-2.0	32+/-1.0	25+/-0.5
Oxidized	>60	46+/-1.2	30+/-1.7

The phagocytal number of alveolar macrophages during the interaction with non-oxidized dust ranges from 2.9 ± 0.18 (jet coal, $K_Ф$ = 1.91) to 1.25 ± 0.11 (anthracite, $K_Ф$ = 9.21) (see Fig.3). Phagocytal numbers measured during the trapping oxidized anthracite and non-oxidized low-rank coal (jet coal) dust particles with neutrophils are almost equal (20.3 and 20.2, respectively) (Table 2).

Table 2

Characteristics of neutriphil interaction with various oxidation degree and coal rank dusts

Dust oxidation degree	Phagocytal number during the coal dust trapping		
	Jet coal ($K_Ф$ = 1.22)	Low-caking coal ($K_Ф$ =6.02)	Anthracite ($K_Ф$ = 9.21)
Non-oxidized	20.2	22.4	26.5
Oxidized	16.8	17.6	20.3

The similar behavior is characteristic for dust trapping with alveolar phagocytes: dust activities of non-oxidized fiery coal (3.2 ± 0.13) and oxidized anthracite (3.2 ± 45) are close. The time of red cell hemolysis for non-oxidized anthracite dust (25 ± 0.5, $K_Ф$ = 9.21) is twice less than low-rank coal (jet coal) dust (50 ± 2.0, $K_Ф$ = 1.22); for middle-rank coal this value is 32 ± 1.0 ($K_Ф$ = 6.02). The phagocytal numbers measured during the trapping dust particles with neutrophils are 26.5 ($K_Ф$ = 9.21), 20.2 ($K_Ф$ = 1.22) and 22,4 ($K_Ф$ = 6.01) for non-oxidized anthracite, low-rank coal (jet coal) and middle-rank coal (low-caking coal), correspondingly.

Table 3

Characteristics of alveolar macrophage interaction with various oxidation degree and coal rank dusts

Coal rank	Coefficient of fibrinigenic activity	Phagocytal number during the trapping	
		Non-oxidized coal dust	Oxidized coal dust
Jet coal	1.91	2.90+/-0.18	4.34+/-0.50
Fiery coal	0.40	3.20+/-0.13	4.58+/-0.31
Low-caking coal	5.21	1.83+/-0.12	3.83+/-0.27
Baking coal	4.24	1.44+/-0.12	3.50+/-0.17
Anthracite	9.21	1.25+/-0.11	3.6+/-0.45

Conclusions

1. The mechanism of an initiating role of coal electrons interactable with oxygen to form biologically active pathogenic species has been established.

2. A method for estimation of coal fibrinogen activity, comprising the determination of the amounts and mobilities of unpaired electrons (from the ESR measurements) reducing oxygen into biopathogenic species has been developed.

3. A considerable increase in biopathogenic activity for non-oxidized coal dust particles compared to that of oxidized coal has been discovered.

4. A complex of methods for the selection, pretreatment and studying of native coals, permitting one to investigate their biopathogenic properties.

References

Berveno V. ESR investigation of gas diffusion in coals. Fuel 1998;77;791-3.