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# An Effect of Treatment by Accelerated Electron Beam on the Composition and Permolecular Structure of Brown and Mineral Coals in a Metamorphism Series

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## Abstract

An effect of the accelerated electrons generated by the electron accelerator on the composition and indexes of the permolecular structure of brown and mineral coals of a metamorphism series has been studied. It has been demonstrated that the effects of ionizing action are controlled to an essential degree by the irradiation conditions and by the stage of coal metamorphism. Middle rank and high rank mineral coals show stability when exposed to an electron beam: their composition, swelling capacity, and the yield of solubles vary a little upon an irradiation with doses up to 200 Mrad. This may be related to the fact that the derivatives of polycondensed aromatic compounds that make up the mentioned coals may cause the radical and ion-radical reactions to decay inside the organic bulk due to the large electron affinity of these derivatives and trapping the low-velocity electrons. Low-rank coals (brown and mineral) with a great deal of aliphatic chains are rather easily subject to the radiation chemical transformations. When absorbing the small dozes (10–50 Mrad), the destruction processes including partial breaking of the valence cross-linking between macromolecules become dominant which leads to loosening the permolecular structure and to an increased capability of interaction with the molecules of organic solvents. The large radiation dozes (more than 50–100 Mrad) promote preferentially the cross-linking processes and structural regularity.

## INTRODUCTION

The coal-chemical research of the last decade pays a significant attention to searching for the effective ways of coal activation in an effort to stimulate the destructive conversions under soft conditions [1]. The development of this direction correlates in many respects with solving the problem of increasing the reactivity of coals and creating the effective technologies of new generation. Most often activation is effectuated by treatment with various chemical reagents as well as through the reagentless mechanical action in the energy-intensive activator mills [2–7].

An effective reagentless method of action upon an organic matter is the high-energy ionizing radiation, which is considered as a means to introduce the high-velocity electrons into a substance [8]. The basic part of energy of these electrons dissipates thus generating a great deal of low-velocity electrons (an energy of the order of several tens and hundreds electron-volt), which initiate the ion-radical reactions through excitation and ionization of molecules. g-Radiation, a-, and b-particles emission during the radioactive nuclear decay are most often applied as the sources of ionizing radiation. However, their technological use presents problems in view of their high penetrating power and investigations of their action upon coal are rather limited [1, 9, 10].

The progress in creating powerful electron accelerators [11] opens up fresh opportunities

TABLE 1

Impact of radiation dose on the composition of brown and mineral coals at different metamorphism stages

| Coal specification, sampling site | Vitrinite reflection index $R_0$, % | Irradiation dose, Mrad | Elemental composition of coal organic matter, % | | | H/C atomic ratio |
|---|---|---|---|---|---|---|
| | | | C | H | (O + N + S) | |
| B, "Kaychakskiy" strip mine | 0.30 | – | 72.5 | 5.1 | 22.4 | 0.84 |
| | | 10 | 71.5 | 4.6 | 23.9 | 0.77 |
| | | 50 | 71.7 | 4.8 | 23.5 | 0.80 |
| LF, "Zadubrovskiy" strip mine | 0.44 | – | 79.7 | 5.8 | 14.5 | 0.87 |
| | | 10 | 77.2 | 5.7 | 17.1 | 0.79 |
| | | 50 | 76.6 | 5.5 | 17.9 | 0.86 |
| | | 200 | 78.1 | 5.8 | 16.1 | 0.89 |
| LF, "Gramoteinskaya" mine | 0.56 | – | 78.6 | 5.6 | 15.8 | 0.86 |
| | | 10 | 77.5 | 4.9 | 17.6 | 0.76 |
| | | 50 | 78.0 | 5.2 | 16.8 | 0.81 |
| G, "Zarechnaya" mine | 0.72 | – | 81.8 | 5.8 | 13.1 | 0.86 |
| | | 10 | 79.4 | 5.7 | 14.9 | 0.86 |
| | | 50 | 79.1 | 5.4 | 15.5 | 0.82 |
| | | 200 | 79.8 | 5.7 | 14.5 | 0.86 |
| F, "Chertinskaya" mine | 0.98 | – | 86.5 | 5.9 | 7.7 | 0.81 |
| | | 10 | 85.6 | 5.8 | 8.6 | 0.79 |
| | | 50 | 85.9 | 5.7 | 8.4 | 0.79 |
| | | 200 | 85.9 | 5.9 | 8.2 | 0.82 |
| LS, "Tomusinskiy" strip mine | 1.56 | – | 88.8 | 5.0 | 6.2 | 0.68 |
| | | 10 | 87.9 | 4.8 | 7.3 | 0.65 |
| | | 50 | 88.5 | 4.7 | 6.8 | 0.64 |
| | | 200 | 88.4 | 4.9 | 6.7 | 0.66 |

for the high-velocity electrons to be introduced in the structure of matter with no use of highly penetrating radiation. Electron accelerators enable increasing the electron energy and, by several orders, the radiation strength. Currently an application of electron accelerators for the technological purposes attracts a steady interest and qualifies as a promising nonchemical means of promoting the petrochemical and coal-chemical processes [1, 12–15] and treatment of the various inorganic materials [16, 17].

This work presents the outcomes of investigation into an action of the accelerated electron beam with energy of 1 MeV generated by the electron accelerator on chemical composition and permolecular structure of coals at different stages of metamorphism.

## EXPERIMENTAL

The investigations were conducted over a wide set of specimens of brown and mineral coals of the metamorphism series that were selected at the Borodinskoye deposit of Kansk-Achinsk basin and at the deposits of Kuznetsk basin. Vitrinite concentrates were selected from Kuznetsk coals (the vitrinite content of 95–98 %, ash content of 1.5–2 %), the composition of which is given in Table 1. Kansk-Achinsk brown coals are represented by two specimens that are essentially disparate in the content of alkali-earth metal cations (with calcium predominant) (Table 2), which, as it has been found in [4], are involved in the formation of permolecular structure of organic matter thus defining its chemical properties in many respects.

TABLE 2

Characteristics and composition of Kansk-Achinsk brown coals

| Sample | Ash content, mass % | Content of ash constituent elements, mass % | | | Elemental composition of coal organic matter, mass % | | | |
|---|---|---|---|---|---|---|---|---|
| | | Ca | Mg | Fe | C | H | N | S |
| $Ka_1$ | 4.4 | 0.75 | 0.10 | 0.10 | 71.3 | 4.8 | 0.9 | 0.2 |
| $Ka_2$ | 6.2 | 1.25 | 0.30 | 0.06 | 70.8 | 4.8 | 0.8 | 0.3 |

Experiments on radiation treatment of coals were performed in the electron accelerator ELV-8 (Institute of Nuclear Physics, SB RAS) in a container with a window from titanium foil. The accelerator generated electrons with energy of 1 MeV; the dosage rate was varied from 0.19 to Mrad/s; the total absorption dose varied from 10 to 200 Mrad. An irradiation was conducted in an inert atmosphere both in the periodic mode by repeated passage of the coal container against the electron beam and with continuous passing of electron beam through coal. The temperature of 7 mm thick coal bed was controlled by means of thermocouple and was maintained in the range of 60–70 and 250–260 °C. Gaseous products evolving during the radiolysis were collected in a gasometer and were analyzed in a chromatograph.

Composition of coals being exposed to radiation was explored by methods of chemical elemental analysis and IR spectroscopy. An elemental composition was determined on the automatic analyser CHN-600 of Leco company. The IR spectra of coal samples within the KBr matrix were recorded with Vector 22 IR Fourier spectrometer of Bruker company in the region of 4000–400 $cm^{-1}$.

The permolecular structure of coals was described from evidence of extraction and swelling in organic solvents and from X-ray diffraction. The swelling of coals was measured by the volumetric method in glass ampoules of 8 mm diameter. Diffractograms were taken in the device DRON-3 with $CuK_a$ radiation. The structural parameters with reference to the ordered graphite-like phase of coal organic matter were defined from the basic reflex (002) [18, 19].

**RESULTS AND DISCUSSION**

An impact of the electron beam on the coal organic matter stimulates chemical transformations accompanied by excretion of volatile matter. Its composition depends on the coal properties, absorption doze, and temperature. The degree of brown coal destruction to volatile products ranged up to 12.8–15.4 %. At 200 Mrad dose and low temperature (60–70 °C), methane (65.9 %) and $n$-butane (23.1 %) prevailed in the composition of hydrocarbon gases that released from dry brown coal (Table 3). When the temperature of irradiation was 250–260 °C, sharp reduction in methane (down to 27.9 %) and $n$-butane fraction (down to 11.8 %) was observed and the content of ethylene, propylene, propane, and isobutane increased. Upon irradiation of the ordinary brown coal containing the native moisture (18 %) at a temperature of 250–260 °C, the methane fraction dropped down to 12.2 % and that of $n$-butane increased to 58.1 %. Presence of $C_5$–$C_8$ hydrocarbons also was found in volatile products. In all cases, hydrocarbons showed predominantly normal structure: accordingly, the content of $n$-butane exceeded the content of isobutane by a factor of 5–10. The excretion of volatile products of destruction was insignificant at a small absorption dose (50 Mrad) and at a temperature of 60–70 °C.

Based on evidence of elemental analysis (see Table 1), carbon and hydrogen content decreases as a consequence of irradiation; the H/C atomic ratio decreases at small radiation doses (£50 Mrad).

Essential changes in composition occurred upon irradiation of brown coals. Intensity of bands in the IR spectra decreased in the wide

TABLE 3

Composition of hydrocarbon gases evolving on exposure of $Ka_1$ brown coal to an accelerated electron beam with 200 Mrad dose, %

| Gas | Coal | | | |
|---|---|---|---|---|
| | Dry | Damp | | |
| | Irradiation temperature, °C | | | |
| | 60–70 | 250–260 | 60–70 | 250–260 |
| Methane | 65.9 | 27.9 | 54.7 | 12.2 |
| Ethane | 8.7 | 12.5 | 14.2 | 4.5 |
| Ethylene | – | 15.2 | – | 2.2 |
| Propane | 2.3 | 17.6 | 3.3 | 8.9 |
| Propylene | – | 12.7 | – | 12.8 |
| Isobutane | – | 2.3 | – | 1.3 |
| *n*-Butane | 23.1 | 11.8 | 27.8 | 58.1 |

region of 1600–1770 $cm^{-1}$ caused by esters, lactones, free carboxylic acids, and the hydrogen-bonded carbonyl groups (Fig. 1). The differential spectra of the samples irradiated with 200 Mrad dose distinctly exhibit the mentioned changes as a negative signal (see Fig. 1, spectra *4, 5*). Initial $Ka_2$ sample incorporated the higher than usual quantity of carboxylates of metals (Ca for the most part), which were detected in IR spectrum by the characteristic absorption in the region of 1520–1570 $cm^{-1}$ (see Fig. 1, spectrum *2*, a shoulder in the band with maximum at 1600 $cm^{-1}$). After an irradiation with 200 Mrad dose, the shoulder decreases that bears witness to partial decomposition of metal-carboxylate groups. Intensity of bands with maxima at 3250 and 2920–2850 $cm^{-1}$, which are due to hydrogen-bonded OH-groups and alkyl substituents respectively, decreases too. Coincidentally with this, the small growth takes place for the intensity of bands at 1040 and 1160 $cm^{-1}$ that correspond to ethers and alcohol. The region of out-of-plane deformational vibrations of C–H bonds of benzene ring is characterized by an increase in the intensity of bands with maxima at 800 and 750 $cm^{-1}$, which correspond to benzene rings with the number of hydrogen atoms in the ring being 1–2 and 4, respectively. Upon 200 Mrad dose irradiation at elevated temperature 260 °C, the peak of absorption band at 1600 $cm^{-1}$ for $Ka_1$ sample is displaced in the

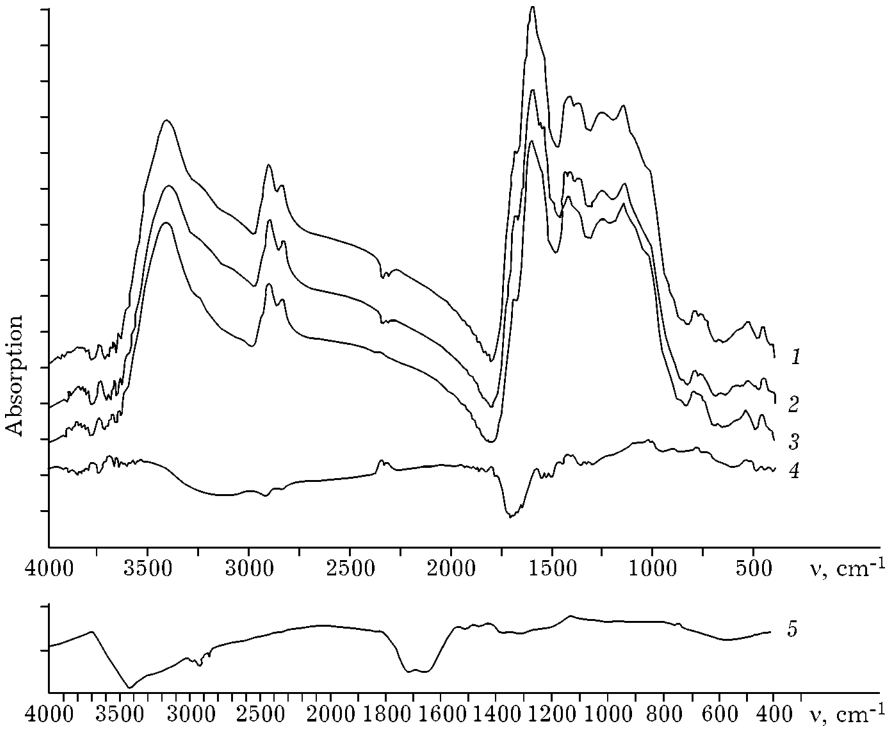


Fig. 1. IR spectra of the initial $Ka_2$ brown coal (*2*) and upon an irradiation by the accelerated electron beam with 50 (*1*) and 200 Mrad (*3*) doze at a temperature of 60–70 °C: *4* – differential spectrum for $Ka_2$ coal (the difference between *3* and *2*), *5* – differential spectrum for $Ka_1$ coal (the difference between the 200 Mrad irradiated sample at 260 °C and the initial sample).

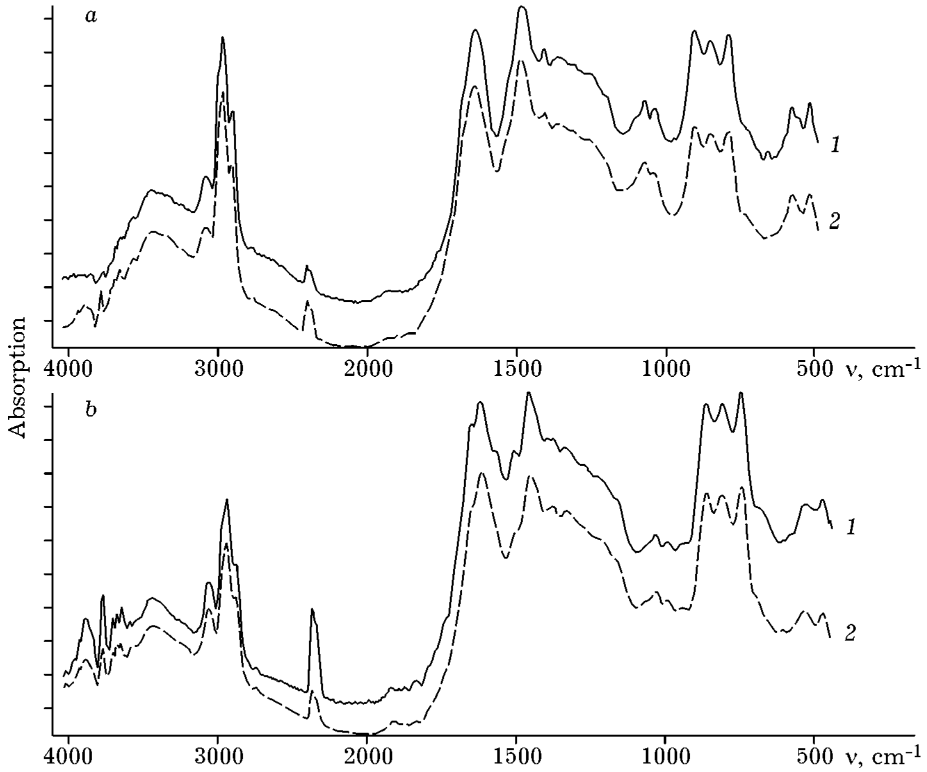


Fig. 2. IR spectra of vitrinites for the initial mineral coals *(1)* of F (*a*) and LS (*b*) specification, and also after irradiation by the accelerated electron beam with a dose of 50 Mrad at a temperature 60–70 °C (*2*).

low-frequency area (by 8 $cm^{-1}$), which can be suggestive of the growing condensation degree for the system of benzene rings. This growth is in a good agreement with stronger absorption in the region of 3040 $cm^{-1}$ that is caused by stretching vibrations of C–H aromatic bonds.

The registered changes in the IR spectra of brown coals suggest that the processes of radiation destruction of ethers and esters, lactones, eliminating of alkyl groups become predominant at small absorption doses. As the dose increases, metal-carboxylate groups also undergo destruction. An increase in the irradiation temperature to 260 °C stimulates the processes of condensation of aromatic cycles.

Composition of mineral coals exposed to irradiation was subject to change to a lesser degree. For the F mark coal, the basic changes in the IR spectra manifested themselves in the reduced intensity of absorption bands of CO groups of ethers and esters (1100–1300 $cm^{-1}$), deformational vibrations of $CH_3$ groups (1380 $cm^{-1}$); to a lesser degree, $CH_2$ groups (1460 $cm^{-1}$), as well as the out-of-plane deformational vibrations of CH groups of benzene rings (690–870 $cm^{-1}$) (Fig. 2). For the deeper metamorphized vitrinite for the coal of the LS specification, composition changes are less distinct. The data acquired bear witness to an increase in stability of organic matter in the metamorphism series upon exposure to an electron beam.

The yield of alcohol-benzene extract from the initial non-irradiated vitrinites in the metamorphism series passed through a maximum for the long-flame coal (Fig. 3, *a)*. Upon irradiation with 50 Mrad dose, the yield of the extract decreased for the low rank vitrinites and changed a little for a middle rank and high rank vitrinites.

Data on the swelling factor reflect the changing density of cross-linking in the polimer-like matrix of the coal organic matter. The swelling factor for the low rank vitrinites (brown and mineral ones) in pyridine substantially increased after irradiation (see Fig. 3, *b)*. No substantial changes were observed for metamorphized coals of F and LS specification.

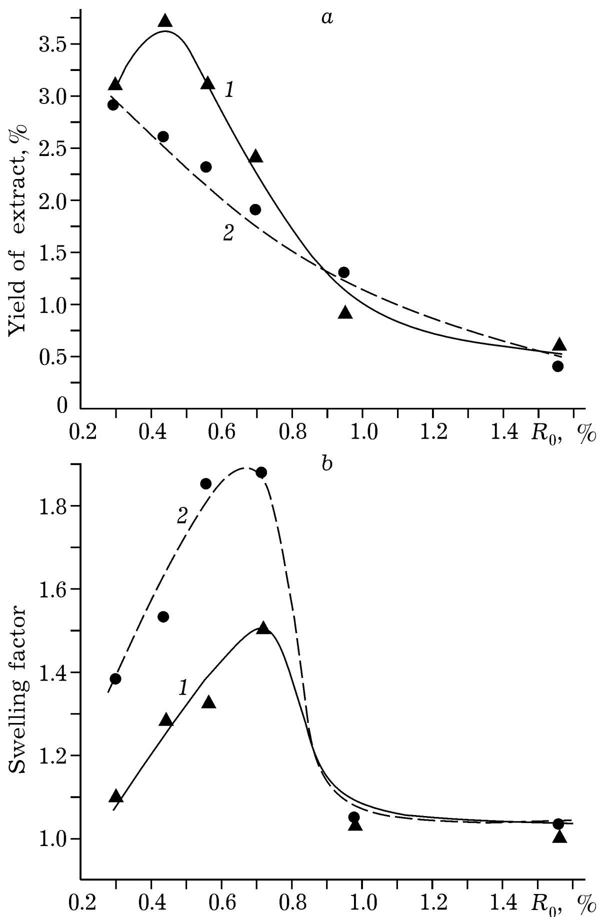


Fig. 3. Yield of alcohol-benzene extract (*a*) and swelling factor in pyridine (*b*) for vitrinite as a function of the metamorphism stage: *1* – initial, *2* – 50 Mrad irradiated.

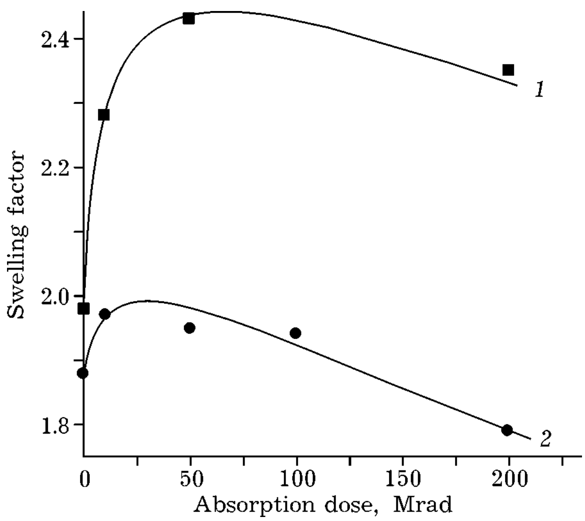


Fig. 4. Change in the swelling factor of brown coals in tetrahydrofuran as a function of absorption doze: *1*, *2* – $Ka_1$ and $Ka_2$ coal specimens, respectively.

Character of dependence of the swelling factor for brown coal in tetrahydrofuran on the radiation dose was different in the small and large dose regions (Fig. 4). The small doses (£50 Mrad) raised the swelling capacity. Further dose increase caused swelling to reduce.

The low-rank coals also exhibited a change in the spatial structure relative to the ordered graphite-like phase under the effect of electron beam. After irradiation of brown coal with dozes of 100 Mrad and less (at 60–70 °C), partial splitting of packages was observed. In the case of $Ka_2$ coal, their thickness decreased from 8.5 to 7.6 Å, and the number of layers in packages decreased from 3.3 to 3.0 (Table 4). Exposition to large radiation dozes (200 Mrad) and temperature of 260 °C, on the contrary, resulted in the integration of packages due to condensation of layers with no change in the interlayer distance.

TABLE 4

X-ray diffraction parameters of the initial and irradiated brown coals

| Sample | Radiation dose, Mrad | Interlayer distance, Å | Package thickness, Å | Number of layers in packages |
|---|---|---|---|---|
| $Ka_1$ | – | 3.7 | 8.8 | 3.4 |
| | 10 | 3.7 | 8.7 | 3.4 |
| | 50 | 3.7 | 8.3 | 3.2 |
| | 200 | 3.7 | 8.8 | 3.4 |
| | 200 | 3.7 | 10.6 | 3.9 |
| $Ka_2$ | – | 3.7 | 8.5 | 3.3 |
| | 100 | 3.7 | 7.6 | 3.0 |
| | 200 | 3.7 | 8.9 | 3.4 |

## CONCLUSIONS

The data obtained testify that the effects of ionizing action of the electron beam are determined to a substantial degree by irradiation conditions and the stage of coal metamorphism. Middle rank and high rank mineral coals are relatively stable when exposed to ionizing action: their composition, swelling capacity, and the yield of solubles vary a little on irradiation with the doses up to 200 Mrad. It may be related to the fact that the basis for these coals is preferentially polycondensed aromatic structures, which, due to their large electroaffinity, are capable of trapping low-velocity electrons. This has the effect of damping the radical and ion-radical reactions.

Low-rank coals with a great deal of aliphatic chains are rather easily subject to the radiation chemical transformations. On absorbing the small radiation doses (10–50 Mrad that corresponds to 25–125 kcal/kg, *i.e.* less than 3 % of coal heat content), the processes of partial destruction of the coal organic matter prevail which includes breaking of the cross-linking between macromolecules. This leads to the formation of the loosened (less cross-linked) permolecular structure, the fragments of which are capable of effective interaction with the molecules of organic solvents. The large radiation doses (more than 100 Mrad) stimulate preferentially the processes of cross-linking and structural regularity.

The regularities we have found for changes in composition and structure of coal organic matter on passage of the high-velocity electrons generated by the electronic accelerator are of interest to effectuate the purpose-oriented modification of their properties with the aim of activation for their subsequent chemical processing.

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