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Effect of Ionizing Radiation on the Organic Components of the Bituminous Coal and Its Subsequent Coking

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Abstract

The effect of ionizing radiation on bituminous coal samples was studied. It was established that pre-treatment of coal leads to an increase in the amounts of oxygenated and asphaltenic fractions in extracts. The effect of ionizing radiation on subsequent thermal destruction of coal was shown. In the process of coking of the treated and extracted coal samples, the yield of coke residues with macroporous structure increased.

Keywords: radiolysis, ionizing radiation, bituminous coal, extraction, thermal analysis, coking

INTRODUCTION

Coking coal of gas (G) and gas-fat (GZh) ranks is a valuable coke-chemical raw material. The processes that are used to obtain liquid and gaseous products from coal involve many stages and require large amounts of reagents.

One of the methods of reagent-free action on the organic mass of coal for the purpose of changing its chemical composition and stimulating destructive transformations under mild conditions is radiolysis based on the application of the radiation: γ -, α -, and β -fluxes generated in the radioactive nuclear decay [1–3]. However, broad use of this kind of treatment is rather problematic because of the risk of radiation pollution.

The introduction of powerful electron accelerators allowing a substantial increase in electron energy and the intensity of ionizing radiation

(IonR) without the use of penetrating radiation may be considered as a promising method to stimulate coke-chemical processes [4–6].

In the present paper, we consider the effect of coal treatment by irradiating with a beam of accelerated electrons on thermal decomposition and coking processes.

EXPERIMENTAL

The effect of IonR was studied with ordinary coal samples from the Ulug bed of the Kaa-Khem deposit (the Republic of Tyva) with particle size 1–2 mm. Coal of 1GRZh rank from this deposit has the ash content of the dry state A^d equal to 6.4 %, analytical moisture content W^a 1.5 %, the yield of volatile substances V^{daf} 47.0 %, lower heating value Q_1^r 6900 MJ/kg. In general, over

the deposit, coal was characterized as low- and medium-ash, low-sulphur, low-phosphorus, with high sinterability. The mass of the samples under investigation was 20 g.

Experiments on radiation treatment of coal were carried out using a linear electron accelerator ILU-6 (BINP SB RAS, Russia): electron energy was 2.4 MeV, the pulse current of the beam 328–330 mA, pulse repetition frequency 2.5 Hz. The samples with the thickness of the absorbing layer less than 1 g/cm² were moved with the speed of 2 cm/s under the outlet window of the accelerator. The doses of radiation treatment were 12.5, 25, 50 and 100 kGy.

The initial intact sample and the sample irradiated with a dose of 100 kGy were subjected to extraction with chloroform in the Soxhlet's apparatus for 7 h. The solvent was removed from the extract using a water bath. The amount of asphaltenes in the substance under extraction was determined by washing the samples with a 40-fold volume of *n*-hexane under ultrasonic action.

The IR spectra of coal samples, residues after extraction, and extracts were recorded using an Infracum FT-801 spectrometer (Russia) within the wavenumber range 4000–400 cm⁻¹ with the resolution of 4 cm⁻¹.

The electron microscopic studies and semi-quantitative analysis of the elemental composition were carried out with a scanning electron microscope (SEM) TM-1000 (Hitachi, Japan) equipped with an attachment with a microanalysis system Quantax 50 (Bruker, Germany).

Coking of coal samples (initial, treated with the IonR, and subjected to extraction) was carried out in a muffle furnace free of air: the furnace with the samples was heated to 850 °C within 1 h, and coking was carried out at a temperature of 850 °C for 1 h.

Thermal analysis of initial coal and the samples treated with IonR was carried out using a differential thermoanalyzer STA 409 (Netzsch, Germany) in the flow of nitrogen (2 mL/min); the weighted portions of samples were above 200 mg, heating was performed up to 1000 °C at a rate of 10 °C/min, platinum-iridium crucible was used. The samples before analysis were not subjected to additional mechanical action.

Raman spectra were recorded with a LabRAM HR Evolution (Horiba Scientific, Japan) spectrometer with the excitation wavelength 532 nm, using a ×100 objective and a diffraction grating with 600 pitches per 1 mm.

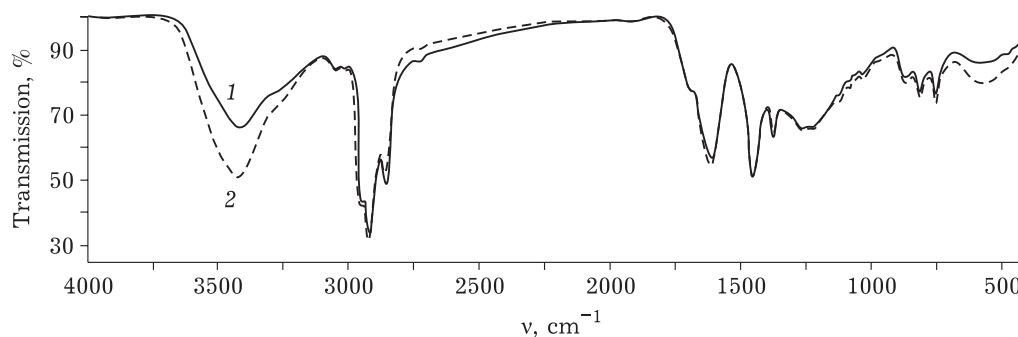


Fig. 1. IR spectra of chloroform extracts from initial coal sample (1) and coal sample treated with IonR (2).

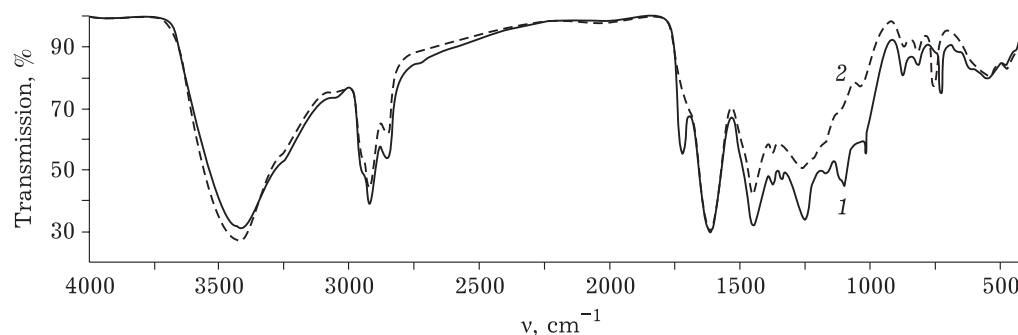


Fig. 2. IR spectra of irradiated coal sample before (1) and after (2) extraction.

RESULTS AND DISCUSSION

Radiation treatment did not cause heating and any exterior changes of the sample; it also did not cause changes in sample mass. The yield of the chloroform extract from the sample irradiated with 100 kGy and from the initial sample was 3.8 and 3.2 % of sample mass, respectively. Fractionation of the extracts showed that after the treatment with IonR the content of asphaltenes in the samples increase from 40 to 60 %. Analysis of the composition of extracts by means of gas-liquid chromatography with mass spectrometry did not reveal any significant differences between the samples. A possible reason may be the presence of many nonvolatile and thermally labile compounds. The IR spectra of the extracts from initial coal and the samples irradiated with a dose of 100 kGy are shown in Fig. 1.

A comparative analysis of the characteristic absorption bands of functional groups in the irradiated coal sample before and after extraction was carried by means of IR spectroscopy (Fig. 2). First of all, aliphatic hydrocarbons are extracted from coal samples (the band at 720 cm^{-1} disappears), along with non-acid carbonyl-containing compounds (a strong decrease in the intensity of the band at 1750 cm^{-1} and a weak change in the intensity at $3700\text{--}3200\text{ cm}^{-1}$), heterocyclic and phenol compounds containing oxy-groups (bands in the region of $1300\text{--}1050\text{ cm}^{-1}$). At the same time, it may be concluded that condensed aromatic compounds remain in the sample to a high extent (the intensity of the band at 814 cm^{-1} changes less than the band at 874 cm^{-1} , and the intensity of the band at 1600 cm^{-1} remains almost unchanged). A band with $\nu_{\text{C-Cl}} = 785\text{ cm}^{-1}$ appears in the spectrum of the solid residue after extraction, which is the evidence of the capture of chloroform by the sample.

The mass of the solid residues of coal samples after extraction increased in comparison with the initial value. No noticeable mass change occurred also during drying of the solid residues at reduced pressure. According to the results of point semi-quantitative analysis involving SEM, the chlorine content in coal samples after extraction changes from 1.2 to 15 % (8 % on average). Chloroform adsorption by initial and irradiated samples after extraction allows us to assume porous and layered structure of the organic substance under investigation.

Four temperature ranges with different rates of mass loss may be distinguished in the thermogravimetric (TG) curves of the samples

under study: 0–400, 400–490, 490–785, and above 785 °C (Fig. 3, a). Mass losses up to 400 °C account for less than 4 % and are connected mainly with the removal of moisture and readily volatile substances. Within the range 400–490 °C, the most intense mass losses occur at 450 °C and are due to the destruction of various types of molecules in the organic matter of coal, those containing the weakest chemical bonds (probably C–O, O–O, S–S). In the case of irradiated samples, more intense mass losses are observed, with jumps at 400–435 °C (see Fig. 3, b). A similar effect was described previously in [7] for thermal decomposition of coal from the Ulig bed of the Kaa-Khem deposit. After 490–500 °C, the decomposition process is observed to slow down for all samples (see Fig. 3, c). Irradiated samples demonstrate lower activity. The observed phenomena may not depict the real situation with thermolysis. The curves of mass loss in the region above 500 °C for samples treated with IonR have a wave-like appearance, which may be due to the non-uniform release of gaseous products as a consequence of pore sealing in the heated sample. Significant mass losses in treated samples occur still after heating is ceased.

Coal samples of G and GZh ranks from the Kaa-Khem deposit are characterized by the increased yield of volatile substances: 42–46 % [8]. According to the data reported in [9], solidification of the plastic mass of coal from the Ulig bed (the transition into semi-coke) occurs within the range 380–490 °C. So, solidification processes hinder the release of volatile components of coal during heating.

The action of IonR promotes solidification at lower temperature, which leads to the emissions of volatile substances. Differences in sample plastification under thermal action are depicted in the morphology of coking products.

An increase in the yield of the coke residue after the treatment with IonR does not correlate with the change in the yield of extracted components. Experiments were carried out to compare mass losses by initial coal and the sample after extraction with chloroform; no significant differences were revealed in the region above 400 °C. The amount of the coke residue after TG investigation, taking into account mass losses due to the intercalation of the solvent at initial stages of heating, differed only insignificantly.

So, it may be assumed that IonR has the most substantial effect on the fractions of the organic matter of coal, strongly bound and not extracted by chloroform.

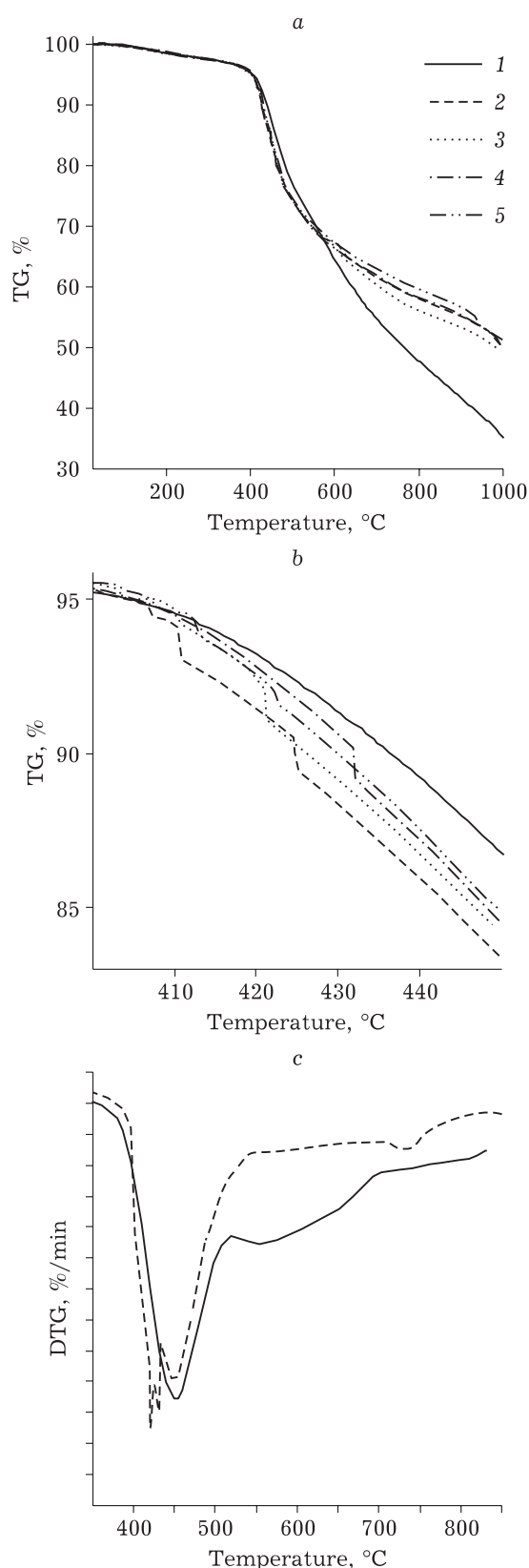


Fig. 3. TG curves within temperature ranges 0–1000 (a) and 400–450 °C (b), DTG curves (c) of coal samples: 1 – initial coal, 2–5 – samples irradiated with the doses of 12.5, 25, 50 and 100 kGy, respectively.

Microphotographs of the surface of coke obtained from initial coal and from coal sample treated with a dose of 100 kGy after extraction with chloroform are shown in Fig. 4. The surface of the coke sample obtained from initial coal is practically smooth and resembles the appearance of a cleaved surface of an amorphous solid body. The surface of coke obtained from the sample treated with IonR and subjected to extraction contains a substantial number of semi-spherical formations, which allows us to assume the mechanism of boiling the volatile substances out by concentrating through the formation of bubbles.

Investigation of the surface with the help of the BET procedure revealed an increase in the specific surface of coke ($\sim 18 \text{ m}^2/\text{g}$) obtained after the action of IonR on coal sample, in comparison with that obtained from initial coal (less than $1 \text{ m}^2/\text{g}$).

Results of Raman spectroscopic studies of coke residues obtained from initial coal samples, extracted coal samples, and coal samples treated with a dose of 100 kGy and then extracted are presented in Fig. 5.

The removal of the organic component during the extraction of coal not treated with IonR does not have any noticeable effect on the degree of ordering of the residues after coking (position, structure and relations between D- and G-bands). At the same time, the treatment with IonR is likely to cause a substantial change in the components that are not extracted with chloroform, which is evidenced by a decrease in the integral intensity of D-band and changes in the region of $2500\text{--}3000 \text{ cm}^{-1}$. An increase in the intensity of the spectra of carbon materials may be due to the existence of secondary ordering [10].

CONCLUSION

Coal treatment with IonR in the air causes some increase in the amount of extractable substances. Polar oxidized compounds dominate in the chloroform extracts of irradiated coal samples. Ionizing radiation also affects subsequent thermal destruction. High-temperature plasticity is likely to increase after the treatment, which hinders the release of gaseous products of destruction and leads to the formation of the macroporous structure of coke residues which possess higher ordering degree according to the data of Raman spectroscopy.

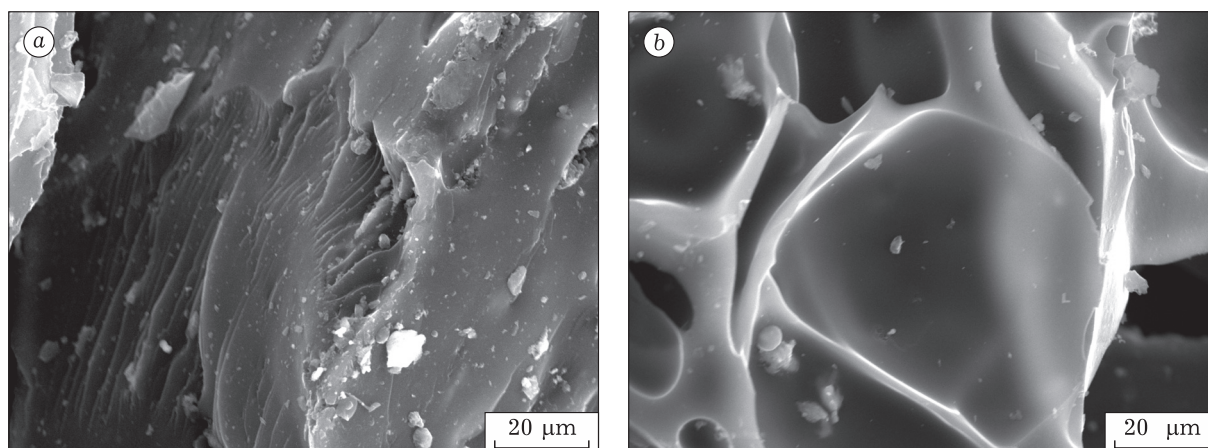


Fig. 4. Microphotographs of the surface of coke residue obtained from initial coal (a), and coal sample treated with a dose of 100 kGy after extraction with chloroform (b).

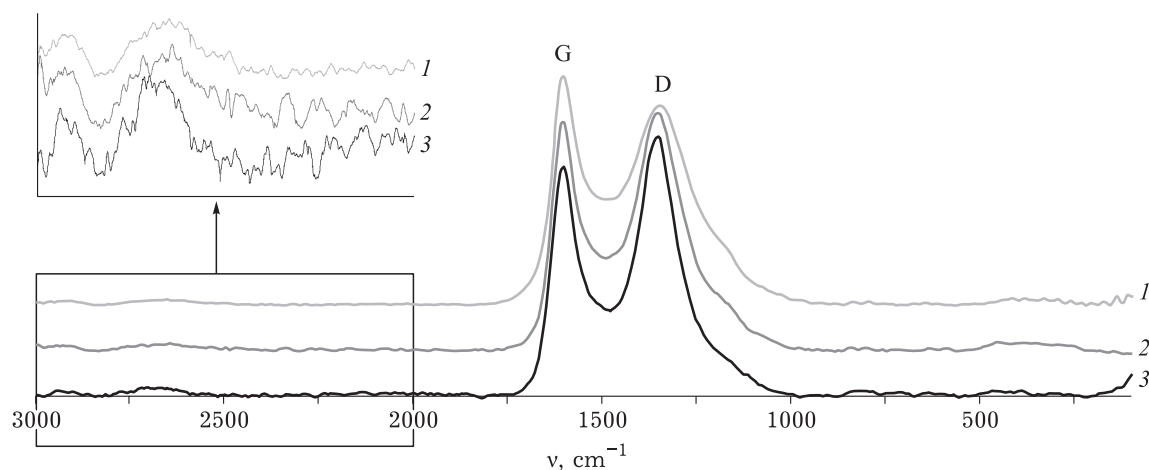


Fig. 5. Raman spectra of coke residues: from initial coal (1), initial coal after extraction with chloroform (2) and coal sample treated with the dose of 100 kGy after extraction with chloroform (3). Insert shows the Raman spectra of these samples within the range 2000–3000 cm^{-1} .

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