

Obtaining the Porous Carbon Materials through High-Speed Heating and Preliminary Chemical Modification of Anthracites

B. N. KUZNETSOV, M. L. SHCHIPKO, N. V. CHESNOKOV, T. P. MILOSHENKO, L. V. SAFONOVA, E. V. VEPRIKOVA, A. M. ZHIZHAEV and N. I. PAVLENKO

Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)

E-mail: bnk@icct.ru

(Received April 5, 2004; in revised form June 2, 2004)

Abstract

To develop a porous structure of anthracites of Donetsk and Kuznetsk basins, two various approaches have been applied: high-speed heating of the grinded raw material in a fluidized bed of catalytically active material in the air flow and thermal treatment in a fixed bed under conditions of thermal shock of anthracite that was previously subjected to chemical treatment. The highest BET specific surface ($653 \text{ m}^2/\text{g}$) and the total pore volume ($0.319 \text{ cm}^3/\text{g}$) are attained at high-speed heating of anthracite that was modified by a mixture of nitric and sulphuric acids. The sorbent yield ranges up to 84 % from the mass of initial anthracite. The produced sorbent shows predominantly microporous texture; its sorptive capacity for iodine (71 %) is at a level of commercial active coals, the obtaining of which requires a long-term energy and resource extensive stage of steam-gaseous activation.

INTRODUCTION

Porous carbon materials (PCM) are used in various industries. With expanding an application range of PCM, the requirements to their assortment, quality, and price increase. Therefore, the investigations into perfectioning of the traditional methods and development of the new methods to obtain high-quality active coals from low-cost kinds of natural organic raw material intensively develop in recent years [1–6].

Traditional raw material for production of quality active coals is the certain species of wood and the shell of coconuts. However, their resources are limited, so the production of active coals from alternative kinds of raw grows. Anthracites that exhibit a high carbon content and the micro- and mesoporosity [7, 8] rank among the feasible and low-cost raw sources.

The most popular method to produce active coals includes two stages: the carbonization of

a starting material and the subsequent activation of the obtained semicoke with gaseous reagents [9, 10]. At the carbonization stage, particular fragments of the organic mass of the solid raw material are transformed to the gaseous state with the formation of pores in the produced carbon material. As a rule, the more is the content of volatile matter that evolves from the starting material during its carbonization, the higher is the pore volume of the carbonized product. Conditions for carrying out the carbonization process act as an alternative important factor, which has an influence on formation of the porous carbon structure. In particular, the low speeds of heating contribute to formation of a microporous structure [10]. At high speeds of heating, a pressure of volatile matter inside the particles of the heated material is increased, which leads to the growing quantity of macro- and mesopores in it [11].

The volatile-matter content of anthracites is low; therefore, the first stage of traditional technology for obtaining active coals (carbonization with slow heating) is optional for them. Meanwhile, it can be assumed that the high-speed heating will allow us to increase a pore volume of the carbon sorbent that is obtained from anthracite.

The autothermal process for obtaining PCM from the brown coal is realized with the use of high-speed heating of the grinded raw material in a fluidized bed of oxidation catalyst [12]. The essence of the process consists in that a powdered fuel is fed to the bottom of a preheated fluidized bed of larger particles of catalytically active material, for example, an open-hearth furnace slag. Having entered the fluidized bed of the slag, the particles of combustible move from the bottom upwards together with air, and thereby they are heated up at a rate of more than 10^3 K/s, are carbonized, and they evolve the volatile matter. The last-mentioned is burnt away on the surface of particles of catalytically active material. Meanwhile, the heat generated provides an

autothermal functioning of the process of coal heat treatment. Duration of the process of coal heat treatment can amount from one to several seconds.

The final stage of traditional technology for obtaining of active coals includes partial gasification (activation) of semicoke by gaseous reagents: steam, carbon dioxide, and oxygen [10, 13, 14]. In this case, pores are formed upon removing the most reactive carbon atoms, which interact with gasifying agents, from the carbon matrix. The maximum development of pore volume is achieved when the process of activation is carried out under conditions of absence from diffusive restraints. If the reactions of carbon with activating agents proceed in a long-range diffusion field, then burning out of carbon occurs along the contour surface of particles with no essential change in their pore volume and specific surface. When the process occurs in the intradiffusive field, formation of macro- and mesopores prevails that adjoin the surface of carbon particles.

High carbon content and rather ordered structure of anthracites determine their low

TABLE 1
Characteristics of anthracite specimens applied

Parameter	Specimen No.				
	1	2	3	4	5
Water content W^r , %	6.8	3.4	1.3	0.5	9.8
Ash content A^d , %	39.7	18.6	29.2	2.9	12.0
Volatile-matter content V^{daf} , %	8.4	7.2	3.6	2.6	5.6
Elemental composition daf, %:					
C	92.6	93.7	94.3	94.4	95.5
H	1.9	1.1	1.6	1.7	1.9
N	0.9	0.8	0.9	1.3	1.1
S	0.7	0.8	1.9	1.3	0.3
O	3.9	3.6	1.3	1.3	1.2
Sieve residue, %:					
-0.315 mm	12.7	1.2	1.4	0.4	0.9
-0.200 mm	84.3	14.5	2.6	1.1	1.4
-0.090 mm	90.1	30.9	7.8	4.2	5.2
-0.063 mm	94.6	38.2	26.2	16.2	19.6

Note. Numbers of specimens: 1 – Donbass anthracite, slimes from dressing, batch 1; 2 – Kuzbass anthracite, batch 1; 3 – Donbass anthracite, slimes from dressing, batch 2; 4 – Donbass anthracite, the enriched product; 5 – Kuzbass anthracite, batch 2. All specimens of anthracites exhibited the total pore volume less than 0.07 cm³/g and specific surface less than 1 m²/g.

reactivity in the processes of steam-gaseous activation. A problem to increase the reactivity of anthracites is solved by means of their chemical treatment. In particular, the literature contains the insights about an increase in the reactivity of anthracites in the steam-gaseous activation processes after their treatment with nitric and chloric acids [15–17].

This work investigates the potentials for obtaining the powder active coals from anthracites by application of two various approaches: high-speed heating of the grinded anthracite in a fluidized bed of oxidation catalyst or the open-hearth furnace slag and thermal treatment of chemically modified anthracite in a fixed bed under conditions of thermal shock.

EXPERIMENTAL

Specimens of anthracites from Donetsk (Ukraine) and Kuznetsk (Russia) basins were used in the experiments. Their characteristics are presented in Table 1. Choosing the subjects of the research is caused by the wide scale of their commercial output.

Before being used, the specimens were grinded in a planetary mill to a pulverous state. The particle size distribution presented in Table 1 corresponds to the specimens that have been grinded.

Carbonization of pulverous anthracite occurred in a setup that is described in detail in the works [12, 18]. The grinded anthracite is fed by air from the bottom upwards through a fluidized bed of larger particles of the fluidized bed material, which has been previously warmed up to a specified temperature. Heat-treated particles of combustible are born with gases from the device and are collected in a cyclone. Aluminum-copper-chromic oxidation catalyst IK-12-70 and the secondary open-hearth furnace slag that exhibits catalytic activity in oxidizing reactions was used as a material of fluidized bed [19, 20]. The catalyst particle size was of about 1.5 mm, the content of copper chromite was 4.8 %. The slag particle size was 0.8–1.2 mm, the content of the basic components, mass %: SiO₂ 9.2, Al₂O₃ 6.9, CaO 38.6, MgO 14.3, MnO 5.7, Fe 8.6.

Reactivity of the heat-treated anthracites was determined by the derivatography method in the air medium. Specimens 35–40 g in mass were heated in a platinum disk crucible at a rate of 2.5 °C/min up to 800 °C.

Chemical treatment of the initial anthracite was performed as follows. A grinded specimen was subjected to the magnetic separation, during which a removal of ferromagnetic component occurred. Then the specimen was heated to 100 °C to transform the diamagnetic component into ferromagnetic one and the magnetic separation was repeated. Demineralization was performed by boiling of anthracite for 12 h in HCl solution; then it was processed with etching acid under stirring for 1 day at ambient temperature, washed out with water, separated from liquid by filtration, and dried at a temperature of 105 °C to constant mass. After demineralization, the percentage of ash in the specimens of anthracite did not exceed 0.5 %.

Chemical modification of demineralised anthracite was made by treatment with the five-fold volume of a mixture of the concentrated nitric and sulphuric acids taken in the ratio 9 : 1. The temperature and duration of treatment were varied in the course of experiments. After treatment, anthracite was brought on the Shott filter and was filtered off in vacuum by means of a water-jet pump; then it was dried at 105 °C, weighed, and analyzed.

Heat treatment of chemically modified anthracite was conducted in a reactor from the stainless steel of capacity 90 ml that was previously heated to 900 °C. A batch of a specimen (0.2–0.3 g) was put into a heated reactor, was closed, and let to stand for 1–3 min.

Registration of IR spectra was conducted in Vector 22 IR-Fourier spectrometer of Bruker corporation within the KBr matrix at a constant concentration of the substance under study. The computer processing of spectral information has been performed using the OPUS 3 code, version 2.2.

X-ray diffraction analysis was made in DRON-3 X-ray diffractometer (LOMO, Russia). CuK_α radiation was used, $\lambda = 1.54056$ nm, accumulation time was 10⁻³ s, an interval was 0.02 deg.

BET specific surface was determined from nitrogen adsorption at 77 K; the microtextural

TABLE 2

Thermoactivation regimes for pulverous anthracite in a fluidized bed and the properties of carbon products

Parameters	Experiment No.			
	1	2	3	4
	IK-12-70 catalyst		Open-hearth furnace slag	
Specimen of raw material*	1	2	3	3
Loading as regards raw material, kg/(m ³ ·h)**	2400	3470	2770	2570
Thermal loading, MW/m ³	1.05	1.02	0.98	1.04
Temperature of the fluidized bed, K	1115	1060	1085	1100
Yield of a solid product, %	85.2	89.0	91.0	79.6
Properties of the heat-treated anthracite:				
ash content A ^d , %	46.6	20.9	32.1	36.7
carbon content C ^{daf} , %	93.6	94.2	92.8	93.0
hydrogen content H ^{daf} , %	1.4	0.9	1.4	1.2
Total pore volume, cm ³ /g	0.21	0.19	0.18	0.17
Specific surface by BET, m ² /g	26	14	27	21

* See Table 1 for the numbers of specimens.

** Presented are the loadings per 1 m³ of the bed filler during rest.

characteristics were calculated from adsorption isotherms of carbon dioxide at 273 K. Vacuum static volumetric automated setup Sorptomatic-1900 (Fisons, Italy) was used for the adsorption measurements.

RESULTS AND DISCUSSION

Thermoactivation of anthracite in a fluidized bed

Experimental data on the anthracite thermoactivation in a fluidized bed of

catalytically active material are presented in Table 2. Under conditions of high-speed heating that are realized in a fluidized bed at heat treatment, approximately twice increase in a pore volume of anthracites occurs, and their specific surface increases by more than an order of magnitude. Nevertheless, the heat-treated anthracites rank much more below than the commercial carbon sorbents as regards these indexes.

However, the preliminary applied heat treatment raises the reactivity of anthracite as regards the gasifying agents. According to the

TABLE 3

Data of derivatographic study of the reactivity for the initial and heat-treated anthracites

Specimen	Characteristic temperature, °C		
	burning point	of the maximum rate of the mass loss	of the complete burning out
Anthracite, specimen 2*	437	566	617
Anthracite, specimen 3*	436	562	621
Heat-treated anthracites**:			
Experiment 2	402	550	600
Experiment 3	404	549	605
Experiment 4	405	551	603

* See Table 1 for the numbers of specimens.

** See Table 2 for the numbers of experiments.

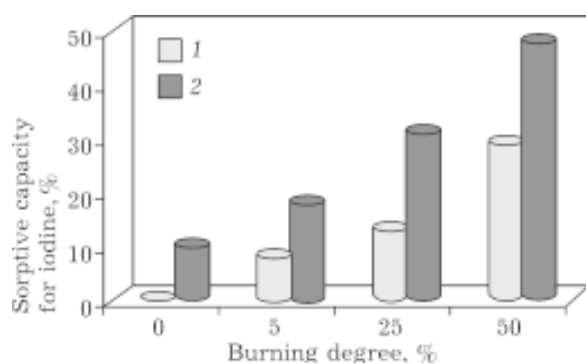


Fig. 1. Sorptive capacity for iodine *versus* the burning degree for the specimens of the initial (1) and the preliminarily heat-treated (2) anthracites. Experimental conditions: initial anthracite is the specimen 2 (see Table 1); it has been heat-treated previously under the regime given in Table 2 (experiment 2) and activated by steam in a steady-state bed at 900 °C.

data of derivatographic study presented in Table 3, air burning point of the heat-treated specimens decreases by approximately 30 °C relative to initial anthracite. For the heat-treated anthracites, the temperature of the maximum rate of the mass loss and the temperature of the complete burning out decrease (by 15–20 °C) too. Upon activation of anthracite specimens that were exposed to the high-speed heating, a preassigned burning degree is reached quicker than in the case of initial anthracite.

As follows from data presented in Fig. 1, the specimens of the initial and heat-treated anthracites that were activated up to identical burning degree tangibly differ in their sorptive capacity for iodine. Depending on the burning degree, the sorptive capacity of the heat-treated and then activated anthracite is more than twice higher than that of a specimen that was activated without prior heat treatment. To yield the sorbents with the identical sorptive capacity for iodine (about 30 %), 16 h is required for treatment of the initial anthracite, and just 4.5 h is required for the thermoactivated one. In addition, during the traditional steam activation, the consumption of the non-activated anthracite comprises more than 2 kg per 1 kg of a sorbent, whereas 1.5 kg of anthracite is required to yield the sorbent analogous in its properties through the thermoactivation stage.

Thus, the preliminary thermal treatment under conditions of high-speed heating in the

fluidized bed allows raising the economy of sorbent production from anthracite.

Heat treatment of chemically modified anthracite

Treatment of a demineralized Donbass anthracite with the mixture of nitric and sulphuric acids at ambient temperature leads to an appreciable increase in its mass. With an increase in the solution/anthracite ratio from 1 to 8 ml/g, the mass of anthracite increases from 16 to 24 % (Fig. 2). The decrease in mass of the specimen that is observed in the further increase of the solution/anthracite ratio is caused obviously by the reactions of deep oxidation of anthracite to form carbon oxides, other gaseous compounds, and water.

An increase in the mass of anthracite during its chemical treatment is related supposedly to the formation of intercalation compounds [21] together with oxygen- and nitrogen-containing functional groups [22]. The availability of the latter in the chemically modified anthracite has been recognized by the IR spectroscopy method.

IR spectrum of chemically modified anthracite (Fig. 3, curve 2) unlike the initial specimen (curve 1) exhibits the new absorption bands arising in the region 1700–1300 cm^{-1} . Absorption bands with maxima at 3030, 1605,

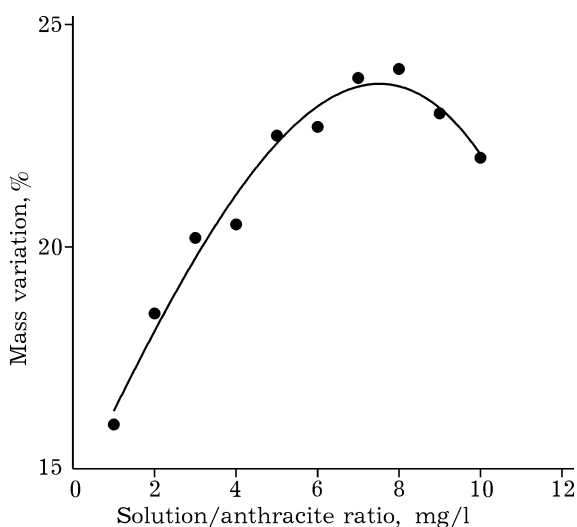


Fig. 2. Changing mass of anthracite (specimen 4, see Table 1) in its treatment with the mixture of nitric and sulphuric acids taken in the ratio 9 : 1. Experimental conditions: the room temperature, duration of treatment is 120 h.

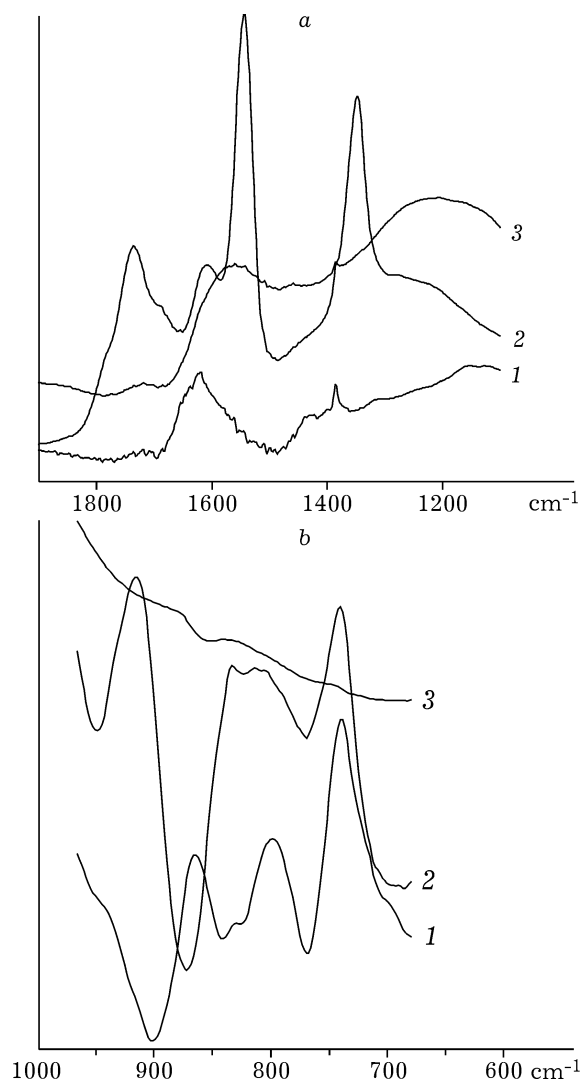


Fig. 3. Fourier IR spectra of anthracite (specimen 4, see Table 1) and of the products of its chemical and heat treatments: 1 - initial anthracite, 2 - demineralized anthracite processed with the mixture of HNO_3 and H_2SO_4 (9 : 1) at the room temperature for 60 min, 3 - specimen 2 after heat treatment at 900°C for 3 min.

and 740 cm^{-1} bear witness to the aromatic structures available in chemically modified anthracite [23]. In addition, out-of-plane deformational vibrations are detected that are characteristic of aromatic H atoms in arenes (900 cm^{-1}) and polynuclear nitroarenes ($\sim 837\text{ cm}^{-1}$). Absorption band at 1734 cm^{-1} that corresponds to stretching vibrations of C=O bond is indicative of carbonyl groups available in this specimen. Intensive absorption bands at 1546 and 1346 cm^{-1} belong to the respective asymmetric and symmetric vibrations of NO_2 group, which forms the bond of the Ar-NO_2

type with the carbon of benzene ring [23]. Analogous results have been obtained by authors of the work [15] in their studying modification of mineral coals with nitric acid. The similar doublet of absorption bands with $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}} = 200\text{ cm}^{-1}$ that is present in the IR spectra of nitrocellulose can serve as an additional evidence for assignment of the mentioned bands to the NO_2 -substituted aromatic fragments of coal organic matter [24]. There are no absorption bands, which are associated with the vibrations of C=O and NO_2 groups, in the IR spectrum of the specimen of chemically modified anthracite that was heat-treated at 900°C (see Fig. 3, curve 3). This may be indicative of their elimination or transformation as a result of heat treatment. The wide absorption bands observable in the IR spectrum are difficult to assign to the vibrations of one or the other of functional groups.

Additional insights into the structure of chemically and thermally processed anthracite specimens have been obtained by the X-ray diffraction analysis method (Fig. 4). The diffractogram of the initial anthracite shows, besides a wide peak in the region of angles $20\text{--}30^\circ$ with a maximum at $d = 3.84\text{ E}$, the distinct lines of pyrite ($d = 2.71, 2.42, 1.634\text{ E}$, JCPDS, 24-76), which die out after demineralization of the specimen. Treatment of anthracite with HNO_3 and H_2SO_4 mixture leads to a sharp decrease in the intensity of 002 peak. This bears witness to a disordering of carbon structure. A short-term thermal treatment of chemically modified anthracite yields a substantial increase in the intensity of the peak that is shifted in the small-angle region and corresponds to the asymmetric maximum 002. However, the intensity of the peak of the initial anthracite is not attained, and this peak in the modified specimen remains wider.

Thus, the diffractogram of the anthracite that was processed by the mixture of nitric and sulphuric acids and then heated at 900°C differs significantly from that of the initial anthracite. A shift of the 002 peak in the direction of small scattering angles occurs and its form becomes bimodal. It is probable that this is suggestive of two types of carbon crystallites that are present in the heat-treated anthracite: the larger ones (that remain from

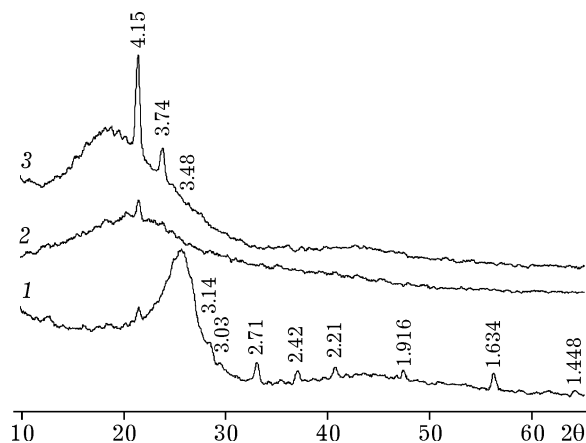


Fig. 4 X-ray diffractograms of the initial anthracite (specimen 4, see Table 1) and of its modification products: 1 – initial anthracite; 2 – product obtained after demineralization and the subsequent modification by HNO_3 mixed with H_2SO_4 ; 3 – the same after heat treatment at $900\text{ }^\circ\text{C}$ for 3 min; figures near the curves represent the interplane distances, E.

the starting material) and the smaller ones (that have arisen upon eliminating the functional groups during the heat treatment of chemically modified anthracite). Clearly crystallized phase with $d = 4.15, 3.74, 3.03$ E can be detected, whose parameters are close to those observed for the chaoite carbon mineral (JCPDS, 24–1069) [25].

The results arrived at are in a good correlation with the data of X-ray diffraction analysis of the modification products for the coals of various metamorphic degree in the system $\text{HNO}_3\text{--Ac}_2\text{O}$. The work [26] demonstrates that the reaction particles (NO_2^+ , AcO^-) that penetrate into a coal skeleton reduce a degree of spatial orientation of structural fragments. The molecular structure is rearranged due to the reactions of nitration, of transformation of aliphatic groups into oxygen-containing groups, and of partial oxidizing decomposition of C–C bonds. It can be assumed by analogy that the basic structural fragments of anthracite modified by the mixture of HNO_3 and H_2SO_4 represent the nitroarenes with N- and O-containing pendent groups, these nitroarenes being aggregated in “crystals”.

The electron-microscopic patterns of the specimen, which was produced through treatment with HNO_3 and H_2SO_4 mixture that was followed by heating at $900\text{ }^\circ\text{C}$ for 3 min, exhibit a spotty contrast on some graphite plates

that might be caused by the effect of heat expansion. The analogous effect was observed upon heat expansion of the intercalated compounds of the natural graphite [27]. Electronic diffraction of these plates matches polycrystalline graphite.

By analogy with thermally expanded graphites, one would expect a substantial development of microporous structure of the modified anthracite upon its heat treatment under conditions of high-speed heating up to $900\text{ }^\circ\text{C}$. BET specific surface of this specimen has been determined from nitrogen adsorption at 77 K, and its microtextural characteristics, from CO_2 adsorption at 273 K. According to computations based on the nitrogen adsorption isotherms, the BET surface is $653\text{ m}^2/\text{g}$, the total pore volume of diameter less than 100 nm is $0.319\text{ cm}^3/\text{g}$, the micropore volume is $0.272\text{ cm}^3/\text{g}$, the mesopore volume is $0.047\text{ cm}^3/\text{g}$, and the average pore size is 2 nm. The method of the density functional theory is applied to analyse the character of micropore size distribution on nitrogen adsorption data [28]. The computations performed bear witness to inhomogeneity of micropores, the width of which in this specimen varies from 0.7 to 2.5 nm, and their average size comprises 0.94 nm.

It is known that the volume of micropores that are less than 0.7 nm in size can be determined from CO_2 adsorption isotherms at ambient temperature. These micropores cannot be registered from nitrogen adsorption at 77 K [29]. Table 4 presents comparative microtextural characteristics of the specimen of the modified and heat-treated anthracite that were calculated from N_2 adsorption isotherms at 77 K and from CO_2 adsorption at 273 K. From the data obtained it follows that this specimen has the developed microporosity. It has practically no micropores less than 0.6–0.7 nm in width. This is indicated, first, by the fact that the volume and the surface of micropores that have been calculated from CO_2 adsorption are less than those calculated from nitrogen adsorption isotherms; and second, by the low value of CO_2 adsorption energy.

The modified and heat-treated anthracite has a high sorptive capacity for iodine, specifically, 71%. Let us note that for the majority of commercial sorbents, this value is no less than 60%. The yield of carbon sorbent from the

TABLE 4

Characteristics of microporous structure of anthracite that was modified by the mixture of HNO_3 and H_2SO_4 and then heat-treated (specimen 4, see Table 1)

Adsorbate	Micropore volume, cm^3/g	Micropore surface, m^2/g	Energy of adsorption, kJ/mol	Width of micropores, nm
N_2	0.272	500	18.4	1.09
CO_2	0.259	345	13.3	1.50

Note. Calculated from data of nitrogen (77.4 K) and carbon dioxide adsorption (273 K) by the theory of volume filling of micropores.

modified anthracite can be as great as 84 % from the mass of initial anthracite, whereas as great as 30–50 % of mass of the starting material can be lost in the course of traditional process of steam-gaseous activation. It should be also pointed out that the use of the new method to develop the porous structure of anthracite does not require a long-term stage of steam-gaseous activation.

Selection of optimum duration of acid treatment at ambient temperature can be made based on the data presented in Fig. 5. Although a tendency for the anthracite specimen mass to grow is preserved during its treatment for several days with the mixture of HNO_3 and H_2SO_4 under the selected conditions, the basic changes occur already in the first 12 h. Thus, the preliminary acid modification of anthracite makes it possible to reduce the duration of heat treatment to several minutes and to raise the yield of the porous carbon product.

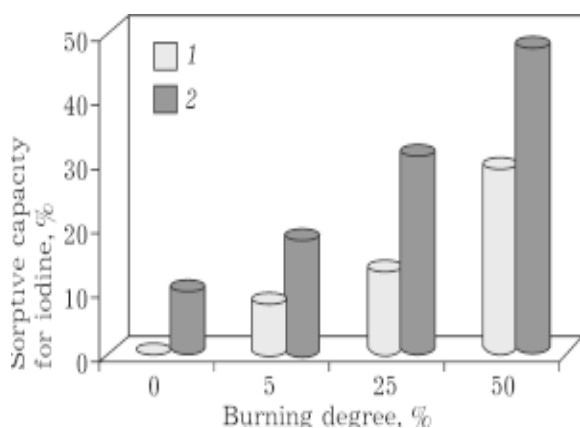


Fig. 5. Effect of duration of anthracite treatment (specimen 4, see Table 1) with HNO_3 and H_2SO_4 mixture (9 : 1) on the change of its mass at the various solution/anthracite ratio, ml/g: 2 (1), 4 (2), 6 (3), 8 (4).

CONCLUSION

In consequence of the completed research, it has been found that the preliminary heat treatment of the grinded anthracite in a fluidized bed of the catalyst or of the open-hearth furnace slag increases its pore volume, specific surface, and reactivity as regards gasifying agents.

Activation of the heat-treated anthracite by steam at a temperature of 900 °C enables one to attain higher indexes of adsorption capacity of the obtained sorbents for iodine with the reduced duration of the process and with the reduced anthracite consumption as compared to the untreated raw material. Interaction of the demineralized anthracite with the mixture of nitric and sulphuric acids at ambient temperature leads to a significant modification of its chemical composition and structure.

The subsequent short-term treatment of the modified anthracite under conditions of high-speed heating up to 900 °C contributes to a significant development of its microporous structure and increases its adsorption capacity for iodine up to the value that exceeds the indices of commercial carbon sorbents. The yield of carbon sorbent from the modified anthracite is twice as much as in the traditional process of steam-gaseous activation, and the duration of activation is just several minutes long.

REFERENCES

- 1 V. F. Olontsev, *Khim. Prom-st'*, 11 (1997) 31.
- 2 D. Lozano-Castello, M. A. Lillo-Rodenas, D. Cazorla-Amoros, A. Linares-Solano, *Carbon*, 39 (2001) 741.
- 3 Takashi Kyotani, *Ibid.*, 38 (2000) 269.
- 4 S. Pusz, B. K. Kwiecinska, S. Duber, *Int. J. Coal Geology*, 54 (2003) 115.

- 5 K. Gergova, S. Eser, H. H. Schobert, M. Klimkiewicz, *Fuel*, 74 (1995) 1042.
- 6 V. V. Strelko, N. V. Gerasimenko, N. T. Kartel *et al.*, *Khim. Tv. Tela*, 1 (2003) 77.
- 7 K. Bratek, W. Bratek, I. Gerus-Piasecka *et al.*, *Fuel*, 81 (2002) 97.
- 8 C. Daulan, S. B. Lyubchik, J.-N. Rouzaud, F. Bequin, *Ibid.*, 77 (1998) 495.
- 9 S. G. Greg, K. S. W. Sing, Adsorption, Surface Area and Porosity, Acad. Press, London, 1982.
- 10 V. B. Fenelonov, Poristy uglerod, BIC SB RAS, Novosibirsk, 1995.
- 11 S. I. Surinova, *Ros. Khim. Zh.*, 38 (1994) 82.
- 12 M. L. Shchipko, B. N. Kuznetsov, *Fuel*, 74 (1995) 751.
- 13 R. C. Bansal, J.-B. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker, New York-Basel, 1988.
- 14 G. M. Plavik, G. N. Troshkin, M. M. Dubinin, *Izv. AN SSSR. Ser. Khim.*, 2 (1994) 231.
- 15 Y. V. Tamarkina, T. G. Shendrik, A. Krzton, V. A. Kucherenko, *Fuel Proc. Technol.*, 77-78 (2002) 9.
- 16 S. B. Lyubchik, R. Benoit, F. Beguin, *Carbon*, 40 (2002) 1287.
- 17 V. Verheyen, R. Rathbone, M. Yagtoyen, F. Derbyshire, *Ibid.*, 33 (1995) 763.
- 18 M. L. Shchipko, *Khim. Tv. Tela*, 3 (1999) 82.
- 19 M. L. Shchipko, S. R. Bogomolov, Z. R. Ismagilov, M. A. Kerzhentsev, *Chem. Sust. Dev.*, 4, 6 (1996) 453.
- 20 B. N. Kuznetsov, M. L. Shchipko, A. V. Rudkovsky *et al.*, Proc. 3rd Eur. Coal Conf., European Coal Geology, in Eran Nakoman (Ed.), Izmir, 1999, p. 325.
- 21 A. Albinak, G. Furdin, D. Begin *et al.*, *Carbon*, 34 (1996) 1329.
- 22 V. A. Kucherenko, T. V. Khabarova, K. Yu. Chotiy *et al.*, *Khim. Tv. Tela*, 4 (1997) 12.
- 23 L. Bellami, The Infrared Spectra of Complex Molecules, Wiley, New York, 1963.
- 24 I. Dehant, R. Danz, V. Kimmer, R. Shmolke, Infrakrasnaya spektroskopiya polimerov, Khimiya, Moscow, 1976.
- 25 Y. Kawai, Myo Than Oo, M. Nakao *et al.*, *Appl. Surf. Sci.*, 121-122 (1997) 156.
- 26 T. V. Khabarova, Y. V. Tamarkina, T. G. Shendrik, V. A. Kucherenko, *Khim. Tv. Tela*, 1 (2000) 45.
- 27 B. N. Kuznetsov, N. V. Chesnokov, N. M. Mikova *et al.*, *React. Kinet. Catal. Lett.*, 80 (2003) 345.
- 28 P. I. Ravikovitch, A. Vishnyakov, R. Russo, A. V. Neimark, *Langmuir*, 16 (2000) 2311.
- 29 D. Cazorla-Amoros, J. Alcaniz-Monge, M. A. de la Casa-Lillo, A. Linares-Solano, *Ibid.*, 14 (1998) 4589.