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EXTREME LOW-GRADE COAL TREATMENT COUPLED WITH X-RAY TESTING

V. Yu. Bazhin[1], R. Yu. Feshchenko[1], G. V. Ramana[2], M. Yu. Shabalov[1]

[1] *St. Petersburg Mining University, Saint-Petersburg, Russia*
[2] *Ardee Hi-Tech Pvt. Ltd, New Delhi, India*

E-mail: bazhin-foil@mail.ru

AUTHOR'S INFO

V. Yu. Bazhin, Doctor of Engineering Sciences, Professor, Head of the Chair of Automation of Technological Processes and Productions
R. Yu. Feshchenko, Candidate of Engineering Sciences, Assistant at the Chair of Automation of Technological Processes and Productions
G. V. Ramana, Doctor of Engineering Sciences, Managing Director
M. Yu. Shabalov, Assistant at the Chair of Economics, Finances and Account

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ABSTRACT

Coal conversion for welding electrode industry and metallurgy is one of the most promising trends as it allows manufacturing products being in higher demand, with the price considerably exceeding the cost of original raw material. Low-grade Kuzbass coal and some kinds of Indian coal, thanks to the structural features, adsorption and ion exchange properties, are of appreciated value as potential raw material for conversion and production for technological, technical and environmental purposes, which calls for the integrated approach to designing dry beneficiation circuits. The authors handle the problem of efficient separation of coal components after cryogenic treatment and further heating in fluid-bed furnaces using classification of solid particles by means of X-ray testing. The resultant coal products can be used in manufacturing welding electrodes and in metallurgical engineering.

Introduction

Russia is among the top coal producers of the world such as China, USA and India. Coal industries in Russia and India possess immense resource potential, however, 70–80% of coal fall under consumers' standards, especially by factors of quality: ash content, moisture content, sulfur content, calorific capacity and caking properties [1]. The low quality of coal considerably abridges the field of coal use in the power, chemical and metallurgical industries. Not more than 30–40% of power-generating coal is subjected to processing in Russia, while in the world, in particularly, in India, nearly all produced power-generating coal undergoes conversion [2].

At the same time, the component composition allows using Kuzbass coal as both fuel and chemical raw material. Kuzbass runs 39 coal preparation plants, half of them using obsolete process flow diagrams of coal dressing by flotation [3]. A major drawback is the need to arrange a huge water-and-slime facility (water treatment, maintenance of water sedimentation tanks, etc., which impairs regional environment.

As an alternative to the current techniques, dry beneficiation of coal enjoys new application in the light of the advanced innovative technologies. Besides the power engineering, coal is required to produce high quality coke used in the metallurgical and chemical industries, starting from ironmaking and finishing with manufacture of anodes and cathodes. Experts forecast that the size of the world market of coking coal will grow not less than by 15 % in the next 10 years [4].

Actually, the scientific problem of dressing of low-grade coal with uniform structure and physicochemical properties remains yet to be solved. This study focuses on efficient separation of coal components at all stages of integrated dry beneficiation using classification of solid particles in the flow pretreated by X-radiation. The integrated preparation of low-grade coal involves cryogenic treatment of coal, first, and, then, heating in fluid-bed furnaces up to the temperature of semicoking.

The review of the literature for the recent 20 years and the studies of patents on alternatives to the dry beneficiation method exhibits deficient knowledge on the consistent kinetic patterns of structural changes in coal.

This study solves the problem of improving dry beneficiation of high-ash and/or low-calorie solid fuel and enhancing its efficiency, considering structural changes in coal.

Experimentation methods and materials

The research included tests on preliminary cryogenic treatment of black coal by liquid nitrogen as the preparatory activating processing. The samples of Kuzbass coal were separated relative to coarseness into two size groups: +1.0 mm and 0.1±0.05 mm. A sample was frozen by immersing in liquid nitrogen (–190–195 °C) under atmosphere pressure for 8–10 min and, then, was placed in a special picture-taking camera. Influence of the treatment on the phase composition and processability of coal was controlled by means of X-ray testing (portable infrared radiation machines UR-20) and final technical analysis of coal (stationary X-ray fluorescence analyzer).

Surface microstructure of coal particles was studied by X-ray microanalysis (DIFEI-402 diffractometer), differential thermal analysis coupled with mass spectroscopy, optical microscopy (Zeiss Axio Lab.A1) and scanning electron microscopy (JSM-6460 LV JEOL with analytical add-on device INCA Oxford). Microhardness of coal samples was tested on microhardness gage PMT-3M, under load of 20 g, in accordance with the standard procedure, and microbrittleness of coal was determined by the number of indents containing cracks [6].

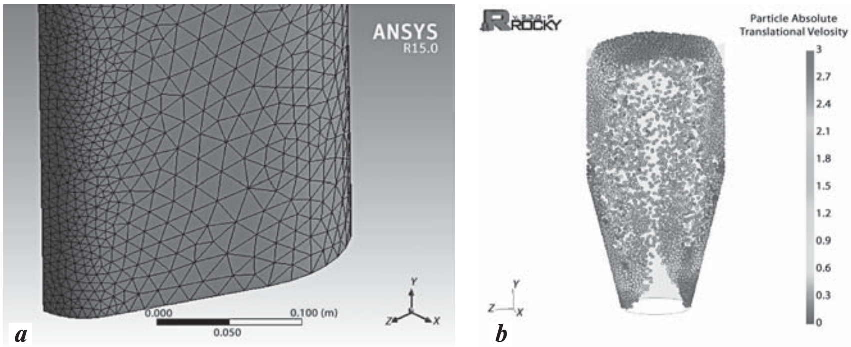

Fig 1. Modeling operating conditions for treatment of granular solid materials in pseudo-liquefied state using adapted programs ANSYS.15 and ROCKY: (*a*) 3D model of fluid-bed furnace, bottom; (*b*) distribution of particles in the reaction chamber of the furnace

Prediction of the velocity distribution and identification of coal particles and ash in gas flow of boiling bed was implemented with adapted programs ANSYS and ROCKY (**fig. 1**). The proposed integrated technology of extreme destruction of high-ash coal includes preliminary cryogenic treatment [7] followed by thermal treatment until low-temperature coking period when charge material transport, processing and removal of particles in gas flow is subjected to X-radiation for separation by flows (**fig. 2**). Classification of particles obeys the procedural rules worked out by the Indian partners from Ardee, India [8]. Preliminary milled coal is placed in a holding tank and subjected to sharp cooling by nitride mixture for internal destruction. The destruction of coal particles proceeds with rupture of interlaminar bonds and structural change of edges; coal particles grow in volume, which enables later separation of carbon and ash using fluoroscopes. After cooling, coal is fast heated in a fluid-bed furnace at a rate of 15–20 °C/s. At the early stage of heating, at a temperature 120–130 °C, moisture is removed, and particles in the flow are broken down to an average size 5–7 mm. At 280–300 °C sulfur escapes intensively, which has beneficial effect on coal quality. The further growth of temperature up to the low-temperature coking stage at 500–550 °C at a rate of 10–12 °C results in bituminization (partial melting of mineral matter in coal) and in sharp structural changes of carbon matrix. Gas mixture fed in amount of 3500–3800 $m^3/(m^2 \cdot h)$ ensures sustainable temperature conditions in pseudo-liquefied bed and efficient separation of mineral matter of coal, which is heavier than coal, accompanied by reduction in ash content (dressing) of the solid fuel produced by the thermal treatment. The next sharp cooling when loading to conveyors for classification by the Agree sort technology allows removal of remaining ash particles and favors the final structuring of coal.

To reach the goal of rational use of coal, it is necessary to determine coal structure as nothing but the structure conditions quality of coal and areas of the most efficient coal dressing. One of the high-performance methods to study supermolecular structure of coal is X-ray crystal analysis. Developed by Russian and Indian scientists, the Agree sort technology of X-radiation of low-grade coal

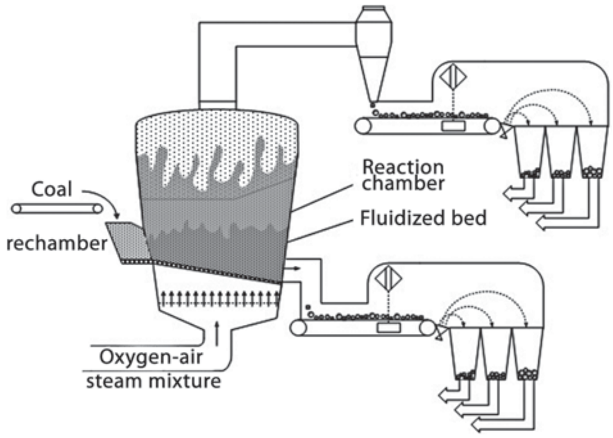

Fig. 2. Dry beneficiation circuit for low-grade coal at the stage of low-temperature coking with separation of particles after X-radiation treatment in accordance with the ArdeeSort technology, India

enables separation of flows during dry beneficiation, control over size of particles and ash content, and partial determination of nature of structural changes in coal under cryogenic and thermal treatment [8, 9].

The method of the dynamic X-ray crystal analysis includes taking of a diffraction pattern of a coal sample and its further processing aimed to determine internal structure of the test sample. The essence of processing is the description of the experimentally obtained dependence by a sum of analytical functions. The X-ray identification and analysis are used in this study for size distribution and further classification of coal particles, determination of ash and sulfur contents under dynamic conditions, and for control over structural changes in coal particles under steady-state conditions. The innovative technology of extreme dry beneficiation is applicable to improvement of Russian and Indian coal quality at preparation plants and in open pit coal mines.

Test results and discussion

The analysis of the samples shows that, depending on a process flow diagram, the sampled materials differ in strength, thermal stability, porosity and reactive capacity. The control over processes and properties requires knowing the entire mechanism of structural changes; for this reason, the study reduces to the theoretical and experimental analysis of physico-technical and chemical-engineering fundamentals of macroscopic and microscopic conversions and reactions of the process.

Preliminary treatment of coal by liquefied nitrogen in a special accumulating tank greatly increases fracturing as compared with the original condition of coal. Cryogenic treatment ensures efficient coal destruction that induces rupture of polyaromatic bonds and swelling of coal under crystallization of external and internal moisture. When coal was placed to a picture-taking camera, it was observed that yield of small size grades had grown by 15–20 % as early as that stage. All grains of coal contained fine cracks over the entire surface of grains. In addition, an increase in microhardness (local strength) by 20–25% was observed at the concurrent decrease in microhardness (plasticity growth) by 15–18%. On the whole, cryogenic treatment results in restructuring of organic matter of coal due to mechanical forces induced, probably, by growth of crystals out of water coal contains [10, 11].

This, to a certain degree, explains an increase in plasticity of coal after the treatment. The coverage and velocity of the described processes govern the fracturing intensity. Cryogenic treatment touches not only organic matter of coal but also alters physicochemical and mechanical parameters of coal, resulting in further growth of fractures, which on the whole contributes to metamorphosis of Kuzbass coal [12]. On the other hand, the induced microcracks ease flow of smaller particles after thermal treatment. It is seen in fig. 3 that the structure of original coal samples has open deformed crystalline layers–bands (**fig. 3**, *a*). Coal samples after extreme cooling both rupture and become chemically active, and readily enter oxidation reactions when in the air, due to the transformation of pore structure, which allows ash removal.

A sample surface after thermal treatment has damages of different degree. For instance, the visible central part has been subjected to more intensive thermal transformation; open pores are seen (**fig. 3**, *b*) and a net-shaped structure is formed. Thermal treatment breaks molecular structure of coal, accompanied by rupture of ether bonds with aromatic cores inside aliphatic structures.

Fast thermal treatment induces complex conversions conditioned both by chemical structure of coal, in particular, its mineral matter mainly between layers composing organic matter, and by heating conditions. As a result, gaseous, vaporous and solid (bitumen) products are formed in different amount and of different composition. Depending on final temperature of heating (pyrolysis) before low-temperature coking (to 500–550 °C), coal becomes softer, volatile matters escape and partly decompose, and pores originate in coal particles (see fig. 3, *c*). Furthermore, morphology of some layers changes, spacing of layers expands and such particles grow in size. Sometimes, fractures appear, and macro- and microcracks initiates.

The dynamic method of exercising control over structure and composition of particles using X-radiation (and special chambers at each levels) in the course of sequential circuits of coal beneficiation was measurement of one or a number of the following characteristics: content of internal and external moisture, ash content, sulfur content, content of each form of sulfur, volatile content, fixed carbon content, traces of minerals in mass, response of coal and its components to electromagnetic emission.

The results show reduction in ash content of some grades of Kuzbass coal after the integrated treatment. It is found that the maximum drop in ash content reaches 40–50% (**fig. 4**). From the processed data on the resultant spectra, percentages of elements were determined. Radiometric methods based on interaction of electromagnetic emission and a test substance are most promising for express-analysis as they ensure prompt measurements essential to exercise control over a process. Gamma-rays and X-rays are most widely applied in practice. Electromagnetic emission wavelengths ranged from metric waves to picometric (10^{-2}) hard gamma-rays. A spectrometer included auxiliary devices for intaking and outputting a sample. The spectrometer supported both manual and automatic control, from

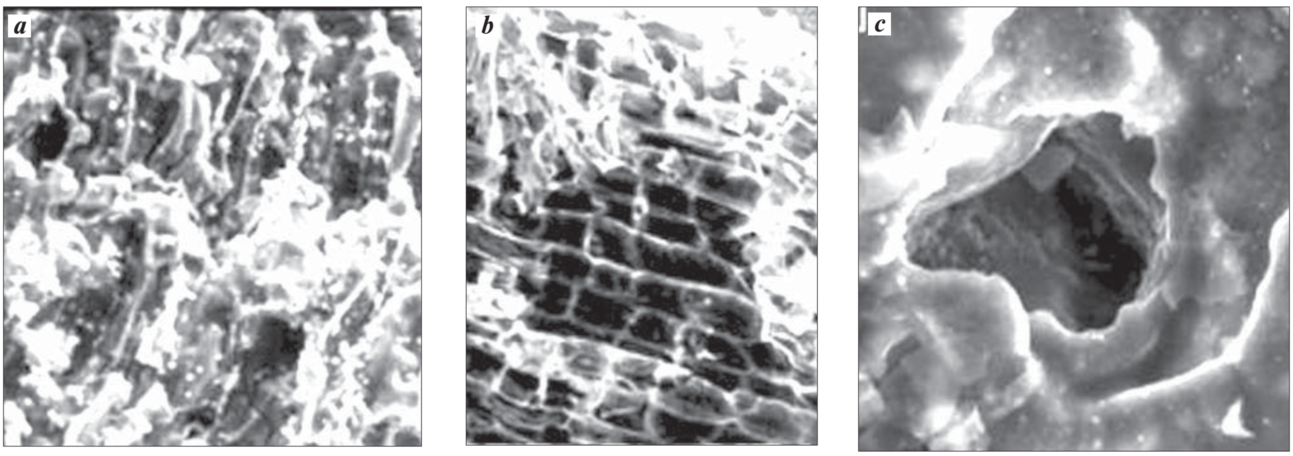

Fig. 3. A surface area of coal sample: (*a*) after cryogenic treatment; (*b*) after thermal treatment; (*c*) after cooling and removal from furnace

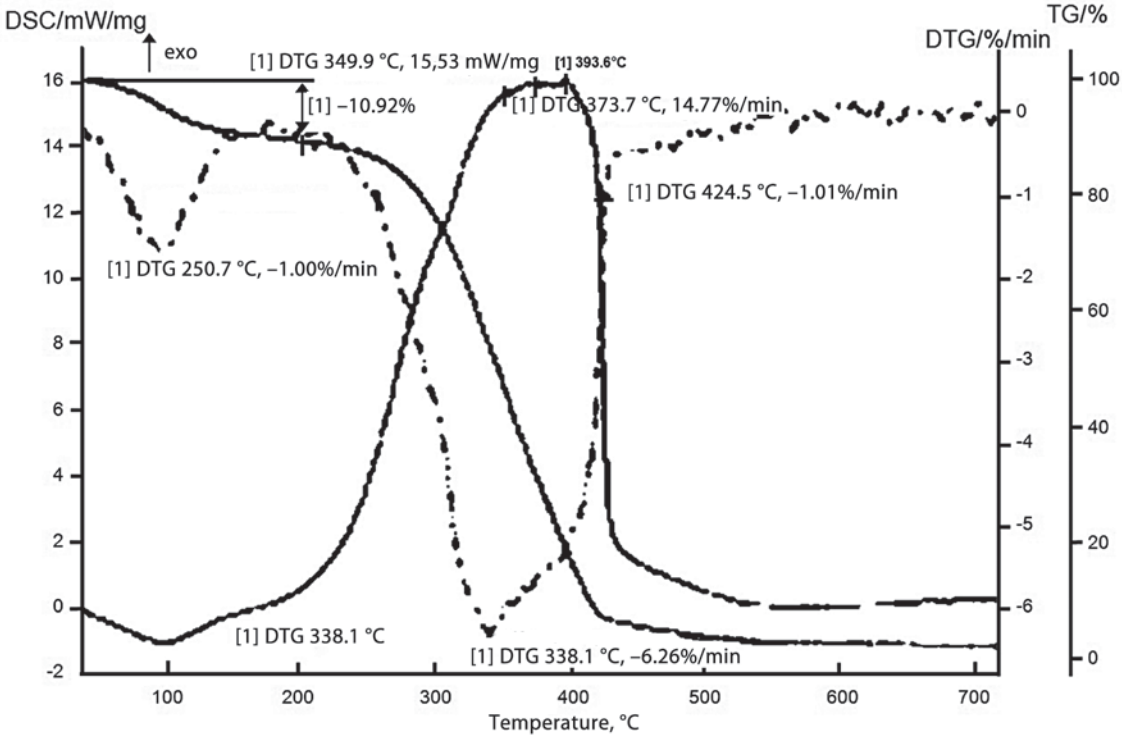

Fig. 4. Data of thermographic analysis of coal surface

a microprocessor or a computer. Scanning and multichannel spectrometers are mutually complimentary, and hold universal and readily resettable analytical programs to handle a wide variety of analytical problems.

The steady-state X-ray fluorescence analysis has shown that an increase in temperature up to the low-temperature coking conditions the end of coal destruction that initiates mechanochemical reactions resulting in breakage of macromolecules of coal and in formation of interlayer pores. Such pores are caused by compaction of matter as sulfur escapes under heating. The data of surface studies of coal samples identify types of pores and their distribution. It is assumable that there are pores that behave as interplane slots through which ash and partial mineral matter are removed when particles collide in boiling bed. The presence of such pores can be connected with the presence of plane aromatic layers in the molecular structure of coal.

It is noteworthy that shear destruction of coal and foliation after extreme cooling and heating in fluid-bed furnace goes with many ruptures of chemical bonds, breakage of organic—mineral compounds and intensification of oxi-destructive processes. Moreover, at the given temperature of heating and extreme cooling, structural changes appear in carbon and ash and they separate. This enables further beneficiation of coal up to reduction in ash and sulfur content at different levels of pseudo-liquefied layer depending on temperature gradient.

Conclusions

An alternative to flotation is dry beneficiation of coal, which finds new efficient application both in Russia and in other countries of the world in the light of the advanced innovative technologies. The economic and technological benefits of dry coal beneficiation offer a background for production of high-quality processable coke using preliminary destruction of coal by cryogenic and thermal treatment, e.g. in fluid-bed furnaces, with change of supermolecular structure, which contributes to incremental removal of moisture, ash and sulfur up to 40—50%.

Development of an innovative technology for extreme thermal treatment of coal aimed to produce high-quality coke based on gas and other-rank low-caking and noncaking coal, and determination of optimal regimes of the processing to guarantee the quality coke (semi-coke) production are the priority economical tasks in Russia and India. To control these processes, it is necessary to know the entire mechanism of structural changes; therefore, the research objective reduces to theoretical and experimental studies into physico-technical and chemical-technological principles of macroscopic transformations and microscopic reactions of the process as a whole.

These studies and the development of new dry beneficiation techniques are evoked by the need for high-quality coke to be produced from cheap and non-deficient coal grades. It has experimentally been found that cryogenic and thermal treatment of coal results in coal breakage and, then, reinforcement. Size distribution of particles and induced fracturing depend on the features of structure and texture of various grades of coal. Being thermally treated, coal exhibits higher microhardness and its microbrittleness rises 2—3 times.

The expected results can be actualized in engineering a pilot plant ensuring output of high-quality coal materials for electrode-manufacturing industry with concurrent use of ash and sulfur.

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REFERENCES

1. Kuzmina T. I. *Ekonomika kompleksnogo ispolzovaniya ugley* (Economy of complete use of coal). Moscow : MGOU, 2010. 250 p.
2. Blagov I.S. (Ed.). *Spravochnik po obogashcheniyu ugley* (Coal beneficiation manual). Moscow : Nedra, 1977. 553 p.
3. *Dolgosrochnaya programma razvitiya ugolnoy ptomyshlennosti* (Long-Term Development Program for Coal Industry in Russia through 2030). Available at: http://www.vedomosti.ru/cgi-bin/get_document.cgi/vedomosti_20-04-2011.
4. Markov V. M., Churasheva N. V. *Ugol v XXI veke: iz temnogo proshlogo v svetloe budushchee* (Coal in the 21st century: From murky past to the bright future). Moscow : Gornaya kniga, 1995. 313 p.
5. Ruban A. D., Lavrinenko A. A., Perederiy M. A. Kompleksnoe ispolzovanie burykh ugley (Complete use of lignite). *Gornyi zhurnal=Mining Journal*. 2011. No. 2. pp. 57–63.
6. *Ugli kamennye I antratsit. Sposob opredeleniya mikrotverdosti I mikrokhrupkosti* (Black coal and anthracite. Method to determine microhardness and microbrittleness). RF State Standard 21206-75.
7. Bazhin V. Yu., Titov O. V. Analysis of the coking process on the basis of heat flux calorimetry. Coke and Chemistry. 2015. Vol. 58. No. 7. pp. 254–258.
8. Ramana G. V. Dry beneficiation of coal — Relevance for Indian coals. CPSI Journal. 2009. Vol. I. No. 1. pp. 35–39.
9. Ramana G. V. Technology for affordable coal quality — Emergence of X-ray on-line solutions. Coal Preparation Technology 2013, Proceedings of National Seminar on Recent Trends and Future Needs in Coal Preparation, CSIR–Central Institute of Mining and Fuel Research, Dhanbad, India.
10. Epshtein S. A. Treshchinoobrazovanie v uglyakh raznykh genotipov (Fracturing in various genotype coal). *Gornyi informatsionno-analiticheskiy byulleten=Mining Informational–Analytical Bulletin GIAB*. 2009. No. 9. pp. 71–76.
11. Podgaetskii A. V., Bunin I. Zh., Epshtein S. A. Vliyanie kombinirovannoy (kriogennoy I elektromagnitnoy impulsnoy) obrabotki na mekhanicheskie svoistva ugley (Influence of coupled (cryogenic and pulsed electromagnetic) treatment on mechanical properties of coal). *Gornyi informatsionno-analiticheskii byulleten=Mining Informational–Analytical Bulletin GIAB*. 2009. No. 3. pp. 159–168.
12. Ivanov V. P., Shkoller M. B., Stankevich A. S. Izmenenie strukturnykh kharakteristik I svoistv kuznetskikh ugley raznoy stepeni metamorfizma I vosstanovlennosti v protsesse ikh okisleniya (Change in structural characteristics and properties of various rank Kuznetsk coal and its reduction degree under oxidation). *Khimiya tverdogo topliva=Solid Fuel Chemistry*. 2002. No. 5. pp. 4–11.