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ON DETERMINING THERMAL CONDUCTIVITY OF BROWN COALS BEFORE AND AFTER THEIR HEAT TREATMENT IN ELECTRIC ARC PLASMA

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ABSTRACT

The paper presents the results of the study of the thermal conductivity of brown coal deposit "Okinoklyuchevskoye" of 0.1-1 mm fraction being processed in an electric arc plasma. To solve the problem there have been experimentally determined actual, apparent and bulk density of coal, as well as its porosity. The research was carried out by calculation based on the model of alternative structures by Misnara, using Fritz B. and H. Moser data. The data received reveal the structural uniformity of the coke residue (activated charcoal), i.e. the degree of its graphitizability.

INTRODUCTION

The development of the science of coals, their technological and power engineering application is characterized by the wide use of physical methods, thermal methods are among them. Their application allows to get more information about the peculiarities of the structure of coals, to assess their energy capabilities, to optimize the process of heat treatment (Agroskin, 1969). Actually the basic process of obtaining the target product from coal of any technical design is thermal degradation (Grjaznov, 1983). To date, the focus is on brown coals reserves which exceed those for coal and anthracite coals in their total aggregate amount. Brown coals are considered not only as an energy fuel, but also as a raw material for the chemical and technological processing to obtain a set of valuable chemicals. In this case, in terms of technology the most interesting is the data on their thermal conductivity and its change during heat treatment, since this property largely determines the duration, efficiency and energy amount of the process (Agroskin *et al*., 1980).

MATERIALS AND METHODS

When processing brown coal for coal and based on them coal char sorbents it is possible to use a plasma arc as an alternative to pyrolysis and retort settings that compared to them significantly reduces activation time, thereby increasing the efficiency of coal processing due to the intensification of the processes of thermal destruction occurring under the action of high temperature, high power density and chemical reactivity of plasma (Buyantuev and Kondratenko, 2012 and Thais *et al*., 1985). In the experiments there has been used the brown coal of the deposit "Okinoklyuchevskoye" with the following characteristics (Table 1), treated with the help of electric arc plasma energy in a modular reactor of combined type (Figure 1).

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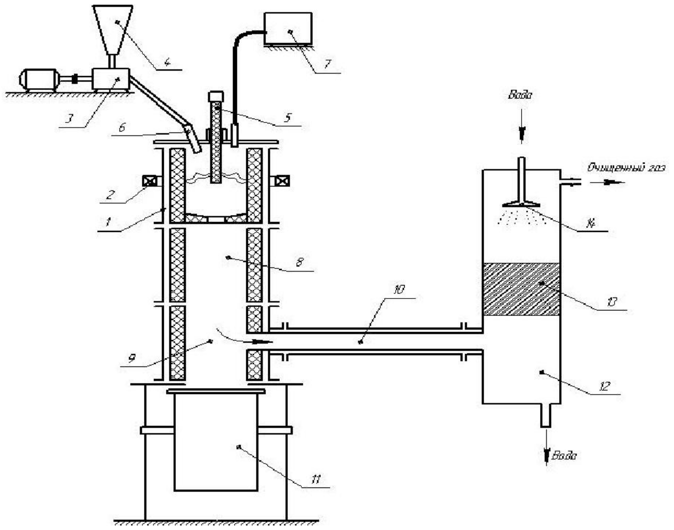
Table 1. Technical and elemental analysis of coal mine "Okinoklyuchevskoye"

Organic mass of coal, % by dry weight					the mineral mass of coal,% by dry weight			
C^c	O^c	H^c	N^c	S^c	SiO_2	Al_2O_3	CaO	Na_2O
64,3	8,45	3,4	0,7	1,52	10,43	4,16	1,33	0,42
	A^a16,40		W^p7,50			V^{daf}45,40		Q_i^r 14,77

where: A^a - analytical ash; W^P - working humidity; Q_i^r - net calorific value, MJ / kg; V^{daf} - volatile substances;

With a uniform rotation of the anode arc spot between the annular anode and the cathode in the reactor core there has been formed the solid plasma environment with an average temperature of 2500-3000OK. Due to this the coal particles fed to the reactor from the top are being completely thermochemically plasma treated. The time of the coal particles staying in the plasma zone depends on the size of the fraction that is adjusted by the aperture in the bottom of the plasma reactor and ranges from 0.1 to 1 sec. The temperature and velocity of plasma rotation is regulated by changing the power supply current of the arc and the arc of rotation of the coil current. While passing through the plasma zone all coal particles are plasma treated for a short period of time accompanied by the pyrolysis and gasification. The solid particles fall onto the bottom of the plasma reactor - the activation cell (Buyantuev and Kondratenko, 2012 and Buyantuev and Starinskiy, 2008).



1 - reactor; 2 - magnetic coil; 3 - dosing; 4- raw materials bunker; 5 - cathode; 6 - ejector; 7 - steam generator; 8 - muffle camera; 9 - separating chamber; 10- gas outlet pipe; 11- solid collector; 12 - scrubber; 13 - filter; 14 - sprinkler.

Fig.1. Plasma modular reactor

The phenomenon of thermal conductivity of solids is the transfer of thermal energy in a not uniformly heated physically homogeneous body. In the one-dimensional steady-state case, this process is described by the equation:

$dQ = -\lambda dT / dx\ dF d\tau$, (1)

where: dQ - the amount of heat transferred during time $d\tau$ through the a read F in the direction of normal x to the site; λ - the coefficient of thermal conductivity; dT / dx - temperature gradient. The minus sign in the right-hand side indicates that the heat flux is distributed in the direction opposite to the temperature gradient.

As follows from the formula (1), the coefficient of thermal conductivity characterizes the permeability of the material for the heat flow. It is numerically equal to the quantity of heat transferred per a unit of area per a unit time at a unit of temperature gradient. The coefficient of thermal conductivity depends essentially on the macroscopic and microscopic characteristics of the material as well as the temperature (Gleybman, 1974).

Unlike the specific heat which is independent of macrostructural factors the coefficients of heat transfer are greatly influenced by the structure heterogeneity. The heterogeneity of the macrostructure of a body is understood as a conglomerate of the basic material (binder) and inclusions of various properties, shapes and size, mostly gaseous or solid. This big group includes various types of powders and filling, porous thermal insulation and refractory, mineral coals, cokes and a number of other natural and artificial materials. On the one hand, the propagating in a not uniform (cracked and porous) body heat flow has to overcome the resistance caused by scattering (binding substance and grain boundary), elongating the way and reducing the "living" section (pores) and finally appearing of discontinuity (cracks). On the other hand, the influence of pores and cracksis to some extent compensated by thermal conductivity of its gas being filled, and (at high temperatures) radiation heat exchange. The convection in the pores of the particulate material is usually negligible (Dulnev, 1970).

To calculate the thermal conductivity of porous materials (coal before and after heat treatment) there has been used a large number of formulas, different in the initial models (Agroskin, 1969; Agroskin and Gleybman, 1980; Mogilevsky and Chudnovsky, 1972 and Kasatochkin, 1975). Some of them do not take into account the influence of radiation exchange in the pores and therefore they can be used at moderate temperatures, or in cases when the thermal conductivity of the binder is so great that part of the radiation contribution is negligible even at high temperatures. To calculate the thermal conductivity the following formula are mainly applied:

1.TheMaxwel's formula, derived for the model "balls laying in the cubic" is as follows:

$\lambda ekv = \lambda 0\ ((2 + \lambda g / \lambda 0) - 2p\ (1 - \lambda g / \lambda 0) / (2 + \lambda g / \lambda 0) + p\ (1 - \lambda g / \lambda 0))$, (2)

where: $\lambda 0$ - thermal conductivity of the binder; λg - thermal conductivity of the gas in the pores; p - the volume concentration of the gas (porosity),a part of a unit.

In the absence of heat transfer in the pores ($\lambda 0$ »λg) the Maxwel's formula is transformed into:

$\lambda ekv \approx \lambda 0\ (1 - p / 1 + p / 2)$. (3)

The Maxwell's formula gives satisfactory agreement with the experiment for small values of porosity.

2. The Roussel's formula:

$\lambda ekv = \lambda 0 (p2 / 3 + (\lambda 0 / \lambda g) (1 - p2 / 3) / p2 / 3 - p + (\lambda 0 / \lambda g) (1 - p2 / 3 + p))$. (4)

3.TheAiken's formula:

$\lambda ekv = \lambda 0 ((1 + 2p ((1 - \lambda 0 / \lambda g) / (1 + 2 \lambda 0 / \lambda g)) / (1 - p ((1 - \lambda 0 / \lambda g) / (1 + 2 \lambda 0 / \lambda g)))$. (5)

gives results coinciding with the ones obtained by the formula (3), if $\lambda 0 / \lambda g$ "1.

4. The Lobe's formula takes into account radiation exchange in the pores:

$\lambda ekv = \lambda 0 ((1 - Pp) + Pp / ((ppr\lambda g) / ((4\psi\varepsilon\nu dav\ T3) + (1 - ppr))))$, (6)

where in: Pp - porosity referred to the cross section. With a uniform pore distribution Pp = p2 / 3; ppr - porosity, referred to the longitudinal plane. With a uniform pore distribution ppr = p1 / 3; ψ - Stefan-Boltzmann constant, which is equal to 5.7 * 10-8 W / (m2 K4); ε - geometric factor; ν - emissivity far; dav - an effective average pore diameter; T - the absolute temperature of the pores.

In the absence of heat exchange in the pores the Loeb's formula becomes a very simple form:

$\lambda ekv \approx \lambda 0 (1- p)$. (7)

According to (Bel'skaya and Tarabanov, 1970), the dependence (7) satisfactorily describes the equivalent thermal conductivity of porous carbon materials with $p \leq 0,5$ in the temperature range 200 - 1700 0C. According to other reports (Kuznetsova *et al*., 1970), the best approximation for graphite high porosity gives the Roussel's formula.

5. The formula of V.I. Odelevskiy for the model of the system with closed cube-shaped inclusions is as follows:

$\lambda ekv = \lambda 0 (1 - p / ((1 / (1 - \lambda g / \lambda 0)) - (1 - p / 3)))$. (8)

When $\lambda 0 \gg \lambda g$ formula (8) gives a result in agreement with the result obtained by the formula (3).

All of the above formulas are derived for the statistically-ordered systems with the translational symmetry.

Thus, A. Misnar considering alternative structures (Misnar, 1968) (a system of continuous solid phase with gaseous inclusions and gas phase with solids) proposed a model in which all actual thermal conductivity of all porous bodies can be represented as a linear combination of the corresponding coefficients of thermal conductivity λ / λ and //:

$\lambda ekv = a \lambda / + b \lambda //$, (9)

where (in our notation):

$\lambda / = \lambda 0 (1 + p ((1 - \lambda 0 / \lambda g) / (1 - p1 / 3 (1 - \lambda 0 / \lambda g))))$; (10)
$\lambda g \lambda // = (1 + B ((-\lambda g 1 / \lambda) / (1 - B1 / 3 (1 - \lambda g / \lambda))))$; (11)

B = 1 - p, a and b - empirical coefficients. According to A. Misnara for coal and coke coefficients a and b are, respectively, 0.4 and 0.6.

To solve the model proposed by A. Misnarom in determining thermal conductivity of coals both in their natural state and after high-temperature plasma treatment it is necessary to use an equation which, with respect to coals before and after heat treatment, can be written as:

$\lambda = 0,4 \lambda / + 0,6 \lambda //$, (12)

where: λ / and λ // - coefficients of thermal conductivity of alternative structures, calculated by formulas (10) and (11). However, assuming that the thermal conductivity of the gas in the pores of coal at room temperature is small, the formula of

A. Misnara are simplified:

$\lambda = \lambda 0 (1 - p2 / 3)$. (13)

Wherein the thermal conductivity of coal λ0 should be taken from Table 2 (16).

Table 2. Thermal conductivity as a function of coalof the actual density d0 (according to Fritz B. and H. Moser)

d_0, , kg / m3	*λ_0, W / (m * K)*	*d_0, kg / m3*	*λ_0, W / (mK)*
1200	0,19	1700	0,96
1300	0,22	1800	1,74
1400	0,28	1900	3,20
1500	0,41	2000	7,33
1600	0,59	2250 (graphite)	163

Therefore, to solve the problem of finding the actual thermal conductivity of coal by equation (13) it is necessary to evaluate their apparent, real density and porosity and to find the coefficient of thermal conductivity from table 2. The apparent density is believed to be the mass of coal together with its pores, so ρk (g / cm3) was determined by gravimetric and volumetric methods. The apparent density of coal ρk (g / cm3) is calculated by the formula:

$\rho k = m1 / m2 - (m3 + m4)$ (14)

where: m1 - mass of coal, g; m2 - mass of water in the amount equal to the volume of coal, wax, and the wire loop; m3 - the mass of water in the amount of paraffin, g; m4 - the same as in the bulk of the wire loop of the density and the mass of wax and wire loop determines the value of m3 and m4. This method is sometimes referred to as hydrostatic weighing. According to test results the apparent density ρk for Okinoklyuchevskoy brown coal before electric arc plasma treatment was: ρk = 1.24 g / cm3. Measurement of the apparent density of large fuel particles larger than 6.5 mm presents no difficulties (Thais and Andreev, 1983).

However, coals subjected to thermal treatment in the vast majority of devices and technologies (pyrolyzer, coke ovens, gasification, hydrogenation device, etc.) must have high dispersion. To study the thermal degradation of coal it is necessary to be able to determine the apparent density of the particles smaller than 2.1 mm. For this purpose, the most suitable technique is (Sainbury and Hawksley, 1968). In the research referred to it has been found that the apparent density of fine particles of coal, both before and after heat treatment (coke) is in exact conformity with their bulk density:

$\rho k = 1.82 * \rho n$ (15)

where: ρn - bulk density of coal.

Measurements made according to the above formula show good convergence of the data with the method of determining the hydrostatic ρk for raw coal. They also give an opportunity to measure ρk of dispersed coal fillings after plasma treatment (Orenbah, 1973). Finding the bulk density of the coal was made by weighing a unit of volume of freely poured coal using jars, mainly measuring cylinders. Coal was poured into measuring cylinders without being pressed but leveled according to the labels. The bulk density of coal ρn (g / cm3) was calculated by the formula:

$\rho n = m1 - m / v$, (16)

where: m - weight of the empty graduated cylinder, g; m1 - the weight of the graduated cylinder with the sample of coal, g; v - the volume of a cylinder filled with carbon, g. Measurement of bulk density ρn of Okinokluchevskoy brown coal yields the value ρn = 0.67 g / cm3 for the raw coal, and ρn = 0.42 g / cm3 for coal treated by plasma.

RESULTS

The results of measurement of apparent density: untreated by plasma samples ρk = 1.24 g / cm3;for plasma treated samples treated for ρk = 0.78 g / cm3. Apparent density values obtained are in good agreement with literature data on research ρk (Thais and Andreev, 1983 and Butyrin, 1976). To determine the actual density of the carbon, both before and after heat treatment thepycnometric method was applied. The essence of this method is to identify in the pycnometer a dense mass linkage coal sample and calculate the density as the ratio of the mass of coal to its volume without pores. The actual density of the coal per dry mass (g / cm3) is found from the formula:

$\rho d = m * (1 - Wa / 100) * \rho r / m * (1 - Wa / 100) + m1 - m2$, (17)

where: m - mass of sample, g .; m1 - weight of pycnometer with a solution of a wetting agent, g (1 g = ρr / cm3) at t = 20 0C; m2 - mass of the pycnometer with a solution of wetting and weight of the fuel, g; Wa - moisture analytical,%.

When making a series of tests to determine the actual density of Okinoklyuchevskoy lignite, before and after treatment with plasma arc the following values of ρd have been obtained: untreated coal ρd = 1.45 g / cm3; coal subjected to thermal effects of electric arc plasma ρd = 1.66 g / cm3. Changing themoisture analytical Wa before and after treatment was observed in the range of 10% and 3%. To determine the effective porosity PEF requires data ρd real and apparent densities ρk coal. Effective porosity is generally expressed as a percentage by the formula:

$PEF = 100 (\rho d - \rho k) / \rho d$ (18)

where: ρd - actual density, g / cm3; ρk - apparent density, g / cm3.

The results of measurements of PEF of raw coal as well as subjected to plasma treatment gave the following results: for the raw coal PEF value = 14.5%, for the coals after thermal degradation in plasma PEF = 53%. Results of definingρd, ρk, ρn and PEF are shown in Table 3.

Table 3. Determination of ρd, ρk, ρn and PEF of Okinoklyuchevskoy lignite before and after the plasma arc treatment

№	ρ_d,g / cm3)	$\rho_к$, (g / cm3)	ρ_n, (g / cm3) (g / cm3)	Pef,%
beforetreatment	1,45	1,24	0,67	14,5
aftertreatment	1,66	0,78	0,42	53,0

For the not thermal treated coal with the apparent density of 1.24 g / cm3 and the porosity of 14.5% of the actual density is ρd = 1.45 g / cm3. In accordance with Table. 2 the thermal conductivity of pores free coal is λ0 = 0,345 W / (m * K). The actual thermal conductivity is: $\lambda = 0{,}345 * (1 - 0.145) 2/3 = 0.311$ W / (m * K).

For the thermal plasma treated coal with the apparent density of 0.78 g / cm3 and the porosity of 53% the actual density is ρd = 1.66 g / cm3. In accordance with Table. 2 the thermal conductivity of pores free coal is λ0 = 0,78 W / (m * K). The actual thermal conductivity is: $\lambda = 0{,}78 * (1 - 0.53) 2/3 = 0.470$ W / (m * K).

Thus, in the coal heat-treated in plasma there is an increase of the thermal conductivity coefficient of its real part being in quasi-homogeneous (non-porous) state, due to the increase of the conductivity of the carbonaceous material, which is associated with a change in its structure (Agroskin , 1969; Agroskin and Gleybman, 1980; Dulnev, 1970 and Van Krevelen, 1960). The study of the parameter λ shows that at plasma processing the coke (activated carbon) becomes structurally homogeneous, i.e. increases the degree of its graphitizability, since molecular structure transformation processes of humites mineral substances are reflected in the change of the thermal conductivity and specific heat of the organic mass (Grjaznov, 1983; Gleybman, 1974; Kasatochkin, 1975; Misnar, 1968 and Orenbah, 1973). In other words, there takes place the three-dimensionally ordered structuring, from fturbostratic amorphous to crystalline regular (graphitizability) characteristic for super anthracites and graphites and indicates an increase in the depth of thermal effect of the plasma upon the material being processed.

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