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The study of specific surface of coal treated by electric arc plasma according to the air permeability data of the layer and the coloring agent sorption

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ABSTRACT

The article presents the results of study of the specific surface area of Transbaikalian coal from "Okinoklyuchevsky" field both before and after heat treatment conducted with the help of two measurement methods: method of the air permeability layer with constant flow rate mode to determine the specific surface area of the coal prior to the transfer to the plasma reactor for thermal activation along with the sorption of coloring agent for studies of coal sorbents undergone plasma processing. In the experiment, we used coal, the sizes of which ranged between 0.1 to 4 mm. Coal passes through a plasma chemical reactor with an arc rotating by magnetic field. Heat treatment of coal in the plasma reactor was performed for a short moment in the water vapor and gasification products (syngas) atmosphere with the process temperatures up to 2500 K0. For the initial determination of the specific surface of the coal prior to the transfer to the plasma reactor, we applied the method of layer air permeability. The basic model of this method is the ratio whereby the rate of flow through a porous medium is proportional to the cross-sectional area and pressure gradient. When calculating the specific surface area of coal entering the plasma activation, it was hypothesized that particles of the latter have spherical shape. In the future, the Sspec determination of the plasma-activated coal was carried out for its use as a sorbent for wastewater treatment. To determine the specific surface of carbon sorbents obtained by arc plasma the technique was used based on sorption of the coloring agent, which involves titration of the suspension of thermo-activated coal quartered samples by 0.3% solution of methylene blue in the sulfuric acid environment. Adsorption of methylene blue gives an idea of surface of the coal past thermal activation in plasma, formed by pores with a diameter larger than 1.5 nm.

Keywords: arc plasma, plasma reactor, specific surface area of the coal, the method of layer air permeability, sorption of coloring agent, thermally activated coal, sorbent, wastewater treatment.

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INTRODUCTION

For studying the nature of coal and solution of some applied problems the characteristics of its specific surface are of great importance. Judging by the specific surface value (S_{spec}, m^2) one can estimate sorption capacity of coals both untreated and heat-treated used for making charcoal sorbents.

Today adsorption is the basis of many industrial operations and research. The most important of them are cleaning, extraction and separation of various substances, gas and liquid adsorption chromatography. Adsorption is an important stage of heterogeneous catalysis and corrosion. Currently carbon sorbent (activated carbon) is used in many processes of chemical technology. In addition, waste gas and wastewater treatment is mainly based on activated carbon adsorption [1].

The basis of the process of obtaining the target product from coal (sorbent) in any of its technical form is heat treatment [2].

The paper studies the change of the specific surface area of Transbaikalian coal from "Okinoklyuchevsky" field both before and after heat treatment conducted with the help of two measurement methods: method of the layer air permeability with constant flow rate mode to determine the specific surface area of the coal prior to the transfer to the plasma reactor for thermal activation along with the sorption of coloring agent for studies of carbon sorbents undergone plasma processing.

EXPERIMENTAL SETUP FOR MAKING CHARCOAL SORBENTS

In the experiment, we used coal the sizes of which ranged 0.1 to 4 mm. Coal passes through a plasma chemical reactor with an arc rotating by magnetic field. At uniform rotation of the anode spot of the arc between the cathode (5) and annular anode (1) a continuous plasma environment with an average temperature of 2000-2500 K^0 forms in the reactor. As a result, the particles of coal that are supplied into the reactor from the top undergo full thermochemical treatment by plasma. The temperature and the rotational speed of plasma are controlled by the change of the current of the arc power source and the current of the rotating arc coil (2).
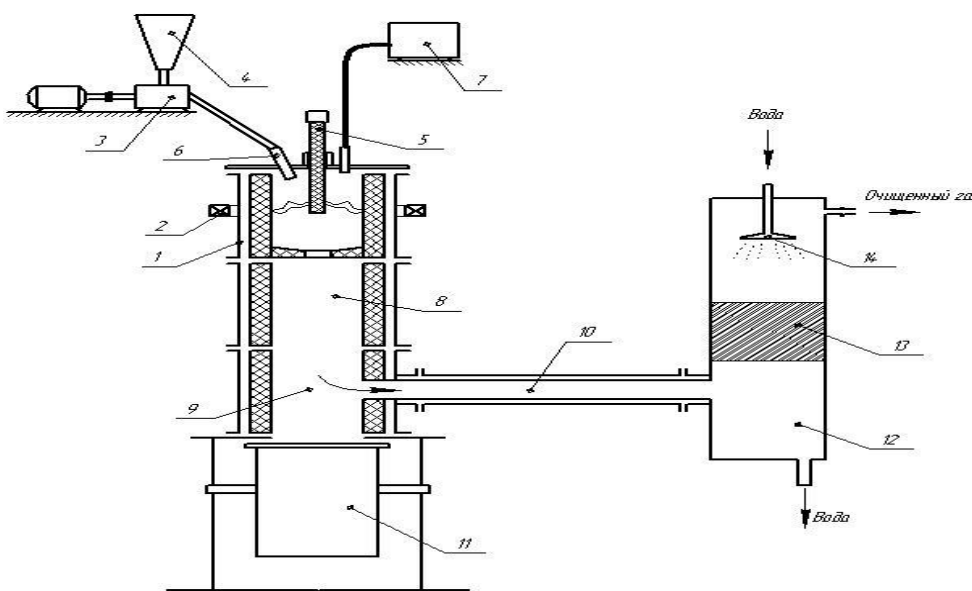

Fig.1. Modular plasma reactor

1 – reactor; 2 – magnetic coil; 3 – batcher; 4 – raw material bunker; 5 – cathode; 6 – ejector; 7 – steam-generator block; 8 – muffle chamber; 9 – splitter; 10 – pipe of the gas tap; 11 – thermally activated coal tank; 12 – scrubber; 13 – filter; 14 – filler.

When passing through plasma zone all the coal particles undergo plasma treatment, a thermal activation occurs.

Solid particles treated by plasma process to the lower part of the plasma reactor – in the coal-tank chamber. The gases formed remove from the reaction zone by an exhaust device. Such principle of plasma systems construction may allow reaching the level of industrial production of coal sorbents and combustible gases [3, 4].

RESEARCH RESULTS AND DISCUSSION

To determine the specific surface area of the coal prior to transfer to plasma reactor we used the method of layer air permeability (Tovarov's method) [5].

The basic model of this method related to the flow of liquid or gas through a porous medium is the ratio installed by Darcy, according to which the flow rate through a porous medium is proportional to the cross-sectional area and pressure gradient.

Darcy's equation has the form:

$$v = k_1 q \Delta P/l, \text{ (1)}$$

where: v is the volume of fluid flowing through a porous medium in unit time; q is the cross-sectional area perpendicular to the direction of the flow; $\Delta P/l$ is the pressure gradient, i.e. pressure drop of the flow ΔP per unit length of the layer l; k_1 – coefficient of proportionality.

Darcy's equation is true for laminar flow of fluid or gas.

As known, any liquid under certain conditions can form a laminar flow; when these conditions are changed, the laminar flow turns into turbulent.

Reynolds showed that the nature of the flow in pipes depends on the average velocity of the fluid u, the pipe diameter D with the viscosity η and the fluid density ρ.

The ratio: $Re = uD\rho/\eta$ determining the character of fluid flow is called the Reynolds number. For cylindrical tubes laminar flow becomes turbulent when the value of Re = 2000.

It is established that in laminar flow for Re the following equation is valid:

$$uD\rho/\eta = k'\rho u^2 l/2Dg\Delta P, \text{ (2)}$$

Where: g – acceleration of gravity; k' is a constant.

From equation (2) the following is obtained:

$$u = 2D^2 g\Delta P/k'\eta l \text{ (3)}$$

If the equation (3) is applied to the direct channel non-cylindrical in shape, for the characteristics of its linear dimensions we use the concept of a hydraulic radius R.

The hydraulic radius R is the ratio of the cross-sectional area to the length of the wetted perimeter, or the ratio of the volume of liquid in the channel to the surface. In this case, equation (3) takes the form:

$$u = R^2 g\Delta P/k\eta l, \text{ (4)}$$

Where: k is a constant.

If the equation (4) applies in conditions of fluid flow through a porous medium, under R we understand the volume of voids divided by the full surface of the particles:

$$R = V - V_r/s, \quad (5)$$

Where: V – the volume of the filtering layer; V_r – volume of particles; s is the surface of the particles.

One of the quantities characterizing the structure of a porous body is *total porosity* P_{tot}, i.e. the ratio of pore volume to the total volume of the sample:

$$P_{tot} = V - V_r/ V, \quad (6)$$

Comparing equations (5) and (6), we obtain

$$P_{tot} V = Rs = RS_{tot}V_r$$

Where S_{tot}– the total specific surface area.
As long as equation (6) implies that
$V_r = V - P_{tot}V$, then $P_{tot}V = R S_{tot} (V - P_{tot} V)$, where:

$$R = P_{tot} / S_{tot} (1 - P_{tot}) \quad (7)$$

Substituting in equation (4) the value of R from equation (7), we obtain the following expression for the average linear flow velocity of fluid (gas) through a porous medium:

$$u = W^2 g\Delta P/ kS_0^2(1 - P_{tot})^2\eta l \quad (8)$$

Volumetric flow rate of fluid v through a porous medium is equal to the product of two quantities – the average linear velocity and the square of the effective cross section. The latter value is expressed by the product of the cross-sectional area q, perpendicular to the direction of flow, and porosity of the filtering layer P_{tot}. Thus:

$$v=uqP_{tot} \quad (9)$$

Introducing in equation (9) the value of $\underline{u}$ from equation (8), we obtain:

$$u = qW^3 g\Delta P/ kS_0^2 (1 - P_{tot})^2\eta l$$

from which:

$$P_{tot} = (gqW^3\Delta P / k\eta v(1 - P_{tot})^2 l)^{\frac{1}{2}}$$

The value k is called the Koceni – Karman constant equal to 5, then:

$$P_{tot} = 14 (qW^3\Delta P / \eta v(1 - P_{tot})^2 l)^{\frac{1}{2}}, cm^{-1} \quad (10)$$

If the total surface is not attributed to the unit volume of the porous object (coal), but to a unit mass, then the specific surface area is:

$$S_{spec}= 14/\rho (qW^3\Delta P / \eta v(1 - P_{tot})^2 l)^{\frac{1}{2}}, cm^2/g \, (m^2/kg) \quad (11)$$

Where: ρ is the density of the substance in g/cm^3.

The obtained equation establishes the dependence between specific surface S_{spec} and volumetric liquid or gas flow through a medium with porosity P_{tot} rate.

The value of total porosity of the filtering layer is calculated by the equation:

$$P_{tot} = (V - m/\rho) / V = 1 - m/V\rho \text{ (12)}$$

Where: V – volume of the filtering layer; ρ – density; m – sample weight taken.

In determining the specific surface area of powder by the method of filtration it is necessary to apply a uniform distribution of the particles so that the gas (air) flows around all particles; moreover, it is necessary to achieve certain caulking, whereby the air flow does not change the position of particles.

For this measurement, the determination of the specific surface of coal was carried out according to the method of air filtering in the device shown in Fig. 2.

The device consists of the following parts: liner 1, plunger 2, pressure gauge 7 and the aspirator (Mariotte flask with a drain stopcock 5) 4.
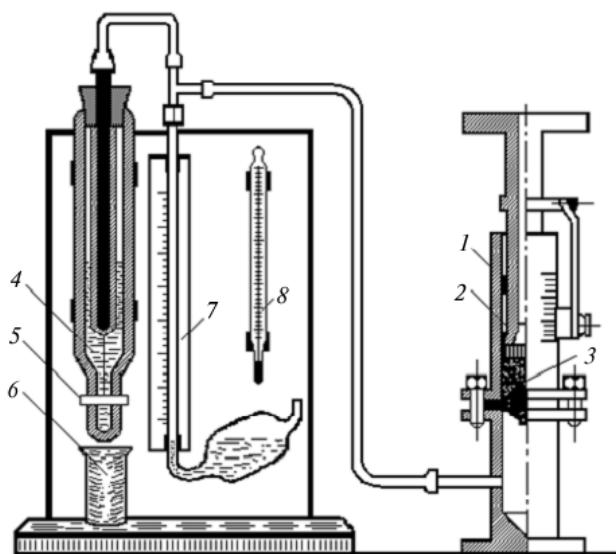

Fig.2 Tovarov's system to determine S$_{spec}$ coal permeability:

1 — liner, 2 — plunger, 3 —powder layer, 4 — Mariotte flask, 5 — drain cock, 6 — cup, 7 — manometer, 8 — thermometer.

The studied coal was placed in the liner and compacted by the plunger, and then we determined the cross-sectional area of the liner q and the volume of the part, in which the powder layer was placed (layer height l).

The table 1 gives the data of layer height, the cross-sectional area of the liner, the weight of test portion and density of coal.

Table 1. Coal layer characteristics

Layer height h, mm	Cross-sectional area of the liner S, cm^2	Weightof test portion	Actual density $\rho_{\text{д}}$, gr/cm^3
19	5	5,670	1,45

Before the measuring, the device undergoes leakage test. After checking, the liner is attached to the unit and drain cock is opened.

When the amount of vacuum shown on the manometer and the water flow rate become regular, we mark the pressure and aspirator fills in a previously weighed beaker, simultaneously setting a stopwatch.

In 1 min we close the valve of the aspirator, and re-weigh the beaker with water, and then calculate the volumetric flow rate v of air, sucked through the layer of powder: $v = m_1 / td_{water}$; where m_1 is the mass of water ejected from the aspirator during the time t. For v measuring the calculation is performed by formula (11). The measurement results are shown in table 2.

Table 2. Data for calculation S_{spec} of Okinoklyuchevsky coal supplied to plasma reactor

Test portion m,gr	Porosity S_{tot}	Flow time t, sec	Water amount m_1, gr	$v = m_1 / td_{water,}$ cm^3/gr	ΔP, cm. wat.st	S_{spec}, cm^2/gr
5,670	0,588	60	92,840	1,55	3,3	800

In the study of coal treated by electric arc plasma, its porous structure data can be obtained from the determination of its specific surface S_{spec} [6]. The study of the surface of thermally activated coal is necessary for further use in various fields of science and technology, in particular for creation of sorbents, catalysts, medicines, etc. on that basis [7].

To determine the specific surface of coal sorbents obtained in the processing of electric arc plasma the technique was used based on sorption of the coloring agent, which involves titration of the suspension of thermo-activated coal quartered samples by 0.3% solution of methylene blue in the environment of sulfuric acid. Specific surface area was calculated based on the number of methylene blue, used for titration of the sample [8].

The test portion of processed coal weighing 1.00 g was placed in a glass with a capacity of 150 cm3, and then we added 20-25 cm3 of water, then the suspension was mixed on a magnetic stirrer, and while stirring we added 1 cm^3 of 5 n (five normal) sulfuric acid. The suspension was titrated with a solution of methylene blue at a rate of 0.1 cm^3 of the solution every 20 seconds.

After surging of each portion of the coloring agent the suspension intensively mixed and then a drop was spilled on chemical filter paper. Titration with the transfer of the suspension droplets on filter paper was continued until the blue colored halo appeared around the dark spots of coal suspension drops. Next we conducted a control test in which the suspension was again intensively mixed for 2 minutes and then a drop of suspension was transferred on a filter. With the disappearance of halo, the titration was continued, if the halo did not disappear, the titration was considered complete, and the appropriate calculations were made.

The calculation of the S_{spec} was performed according to the formula:

$$S_{spec} = (V * C * N_a * A_m) / m * m \text{ or}$$
$$S_{spec} = 6{,}0 * V, \text{ m}^2/g, \text{ (13)}$$

where: V – volume of methylene blue solution used for titration, cm^3; C–the concentration of methylene blue, used for titration, cm^3; Na – Avogadro's number, equal to $6{,}023 * 10^{23}$, 1/mol; Am–the area occupied by one adsorbed methylene blue molecule in close-packed film on the surface of coal particles, is equal to $106 * 10^{-20}$, m^2; m – mass of the treated test portion, g; M – the molecular weight of methylene blue of 319,9 g/mol.

The results of measuring of the specific surface of thermally activated coal determined by the parameters of electric arc plasma system are shown in table 3.

Table 3. The results of S$_{spec}$ of coal processed in a plasma reactor measuring

№	Preconditions				
	I_d, A	U_{ist}, B	G_{coal}, kg/hour	G_{steam} kg/hour	S_{spec}, m^2/gr
1	100	200	50	4	53
2	120	205	50	4	82
3	140	205	50	4	121
4	160	210	50	4	176
5	180	220	50	4	205

Based on the table data, it can be seen that the largest surface area is possessed by the coals, activated when I_d = 180 A but since this kind of processing requires relatively high-energy costs, it is suitable to use the modes # 3 and # 4. In the process of the sorption tests, it was found that the coal activated in plasma during backfilling in water (regular tap water was used), was divided into fractions: the "heavy" (high-ash) fraction, quick settling to the bottom, the fraction of "average" wettability located in the water column, as well as a small portion of the coal particles forming the "light" fraction, popping-up on the surface of the water. Analysis of sorption properties showed that "heavy" (sinking) and "average" (soaring in water column) fraction show good chemisorption properties and "light" (pop-up) fraction has good oil-attracting properties.

Hereafter the study of the possibility of applying the thermal activation obtained porous coal for wastewater treatment was carried out. It should be noted that all wastewaters are a complex heterogeneous system, usually contaminated with various substances, presented in different states, namely: undissolved, dissolved and colloidal. Also all wastewaters are of organic, inorganic and biological compounds by composition.

Initially, we studied the fraction up to 1 mm, but due to the small weight the fraction popped up, so it was carried away with waste water, making it impossible to use this fraction.

At the next phase of the research a fraction from 1 to 4 mm was taken. For the tests, we used the water sample before chlorination; the sample was tested before and after passing through a column of activated charcoal. The results of the research of wastewater before and after purification are presented in Table 4.

Table 4. The results of the research of wastewater before and after purification

Chemical substances, mg/dm^3	Without sorbent	After passing through the sorbent	Purification, %
Ferrum	0,08	0.04	50
Nitrite	0,144	0,0395	72
Nitrate	21,90	11,48	48
Phosphate	2,20	1,73	21
Ammonia	0,34	0,105	69

Industrial tests showed the principal suitability of plasma-treated brown coal as a sorbent for removal of harmful wastewater. The relevance of the tests is also determined by the fact that the presented purification methods are based on local coal resources, expanding the range of their potential use.

CONCLUSION

One of the most common adsorbents (absorbers) is active coal derived from brown (hard) coal. Normal (untreated) coal, or raw coal, has a very low sorption capacity, since the value of its specific surface is small (Table 2), the pores are mostly closed or filled with resins and gases.

Adsorptive power of coal increased with the processing by steam at high temperatures in a plasma environment. As a result of this treatment, the specific surface area of coal increases significantly (Table 3), in this regard the products of incomplete combustion (particularly resins, gases, etc.) are mostly gasified and disappear, it leads to the liberation of pores and increase in the active surface.

Coal sorbents samples with the fractions of 1-4 mm, obtained by electric arc plasma, showed good chemisorption properties (Table 4), which allows to make a conclusion about expediency of its use as sorbents for wastewater treatment and water treatment.

ACKNOWLEDGMENT

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