SIMULTANEOUS DETERMINATION OF THERMAL CHARACTERISTICS FOR DISPERSE MATERIALS IN THE PROCESS OF HEATING

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A relative method is proposed for the direct determination of the set of thermal characteristics for the free-flowing masses of materials in the process of heating, said method based on the application of the principle of a diathermic shell.

No methods are currently available for the direct determination of the entire set of thermal characteristics of disperse materials during the actual heating process [1]. The existing indirect methods of determining the thermal characteristics of the substances—the methods of thermographic calorimetry, based on the use of a so-called diathermic (standard) shell—make it possible to determine the above-mentioned characteristics on the basis of the known characteristics of the diathermic shell [2, 3] or of the standard material [4].

The Barskii method [2], based on the principle of measuring the heat flow directly, can be used to determine the temperature relationship between the heat capacities for small quantities of a material which, in principle, can be heated in accordance with any given law. This method has also been used in another application—to determine the heat capacity and coefficient of thermal conductivity for more substantial quantities of material. However, in this case the material cannot be in the pulverized state, and a special heating regime is used.

Berg and Yagfarov used a quasi-steady heating regime [4] to determine the thermal constants of the materials in bound form. The positive aspects of this precise relative method are the following: no need for calibration of the insulation, which was mandatory in the Barskii method; elimination of the effect resulting from changes in the constants of the actual shell on the nature of the recorded readings; and finally, the ability to use simple calculational formulas. The thermal constants for the materials were determined in this manner up to 300° C. To determine the effective value of the specific heat for a coal load, Agroskin and Goncharov [5] developed an installation based on the Barskii method. The drawback of this installation is the impossibility of using it to determine the remaining thermal characteristics of the coal load.

Here we propose a simple method of determining the thermal constants of a free-flowing load of material which is in the process of being heated. This method is also based on the application of the principle of the diathermic shell, but it is a relative method, thus eliminating the need for preliminary calibration of the thermo calorimeter.

Unlike the Berg and Yagfarov method in which we are actually dealing with two standard materials—material with zero heat capacity (air) and the actual standard material (a comparison of the properties in the test material and the standard is carried out by comparing these against the properties of a material with zero heat capacity)—in the proposed method, the test material is compared directly against the standard.

A general diagram of the installation is shown in Fig. 1; an individual container [cell] is shown in detail in Fig. 2. The installation of the cells presupposes the establishment of conditions making possible a radial influx of heat both to the standard material and to the test substance. The thickness of the diathermic shell and the thickness of the layer of material in the beakers are approximately the same, i.e., 7 and 8 mm, respectively. We have chosen these thicknesses because the installation is intended for the determination of the coal-load properties (when heated, coal changes into a plastic state which spreads through a bed of specified thickness which, for the coal being investigated, amounts to 8 mm). On the other hand, to facilitate automatic temperature recording, the temperatures being measured by the differential thermocouples must be approximately of the same order of magnitude.

The special design of the beakers into the test substances are poured, and the method on the basis of which the junctions of the differential thermocouples are distributed within the cell, make it possible to determine the heat capacity and the coefficient of thermal conductivity for the test substance without resorting to special heating regimes.

The materials employed in the fabrication of the insulation—as well as its design—make it possible to determine the temperature relationships between the thermal constants of the substances when the latter are heated to 600° C.

Many materials—particularly coal—undergo a change in volume when heated, i.e., shrinkage. In the case of coal, the shrinkage and the processes resulting in shrinkage (intense destruction of the coal and the related liberation of gases and weight loss) set in approximately at 400° C. At these temperatures, the disruption of heat-transfer conditions at the boundary between the beaker and the test material—resulting from the formation of a shrinkage clearance between the beaker and the coal—may distort the resulting data. To eliminate the effect of shrinkage, the test

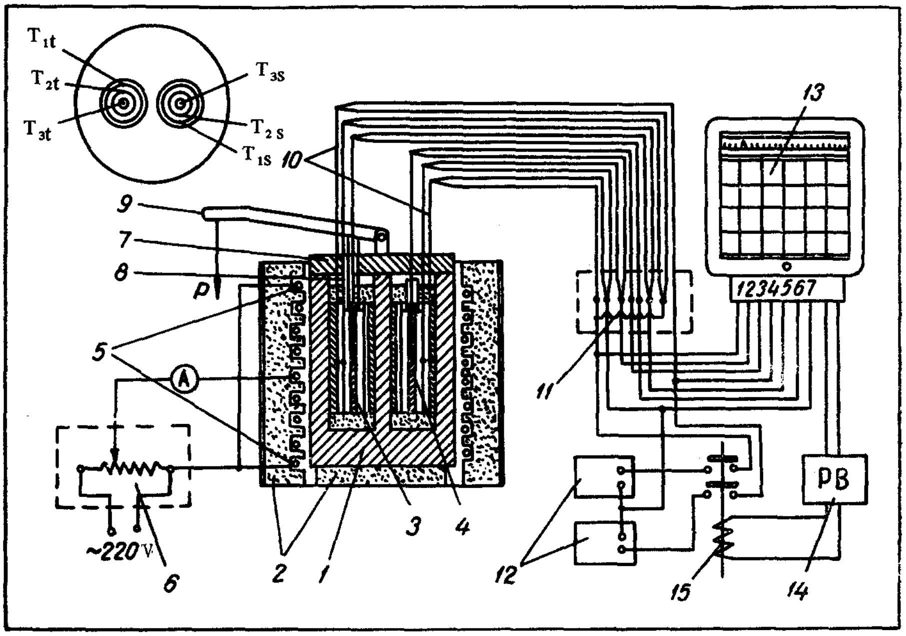

Fig. 1. Diagram of experimental installation. 1) Steel block; 2) thermal insulators; 3 and 4) containers to house the test material and the standard (see Fig. 2); 5) heater spiral, consisting of two face-to-face connected sections; 6) voltage regulator; 7) block cover; 8 and 9) piston and device to apply pressure to the piston; 10) thermocouples (KhA, diameter 0. 2 mm); 11) thermostated space; 12) MSR-58 resistance boxes; 13) EPP-09 potentiometer with modified bridge circuit; 14) electronic time relay; 15) electromagnetic relay; in the upper left-hand corner, a top view of the steel block with the containers, showing clearly the sequence of thermocouple location; the thermocouples are connected to potentiometer 13 in the following manner:

Lead number	1—2	2—3	7-1 shunt	4—5	5—6	7-4 shunt
measured temperature	$T_{1t}-T_{2t}$	$T_{2t}-T_{3t}$	T_{1t}	$T_{1s}-T_{2s}$	$T_{2s}-T_{3s}$	T_{1s}

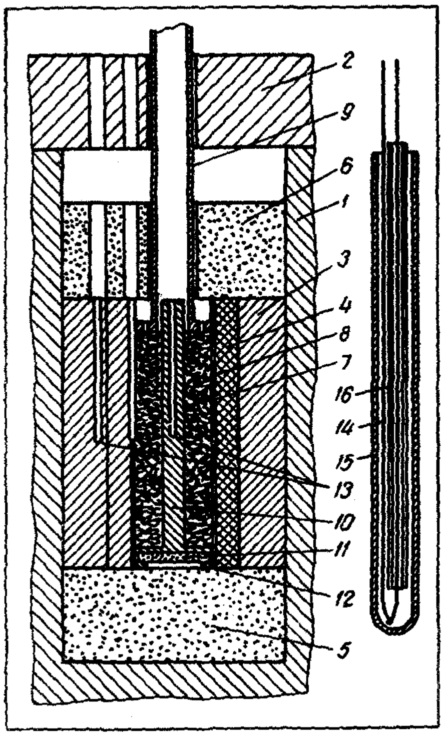

Fig. 2. Design of an individual container [cell]: 1) steel block; 2) block cover; 3 and 4) hollow steel cylinder into which a light weight brick diathermic shell has been pressed; 5 and 6) thermal insulators; 7) steel beaker into which the test (standard) material is poured; a special "pocket" for the thermocouple has been welded to the beaker (the thickness of the beaker wall is 0.25 mm); 8) test (standard) material; 9) piston made of high-melting glass; 10) steel cylindrical rod; 11) asbestos layer; 12) removable ring; 13) thermocouple "pockets" (inside diameter 1.7 mm); 14) thermocouple; 15) external high-melting glass housing (diameter 1.6 mm); 16) glass insulation capillary.

material is placed beneath a special piston which exerts a pressure, so that it descends as the volume of the material is reduced. It thus becomes possible to avoid the distortion of the results which follow from the shrinkage, thereby retaining constant conditions of heat transfer at the boundary.

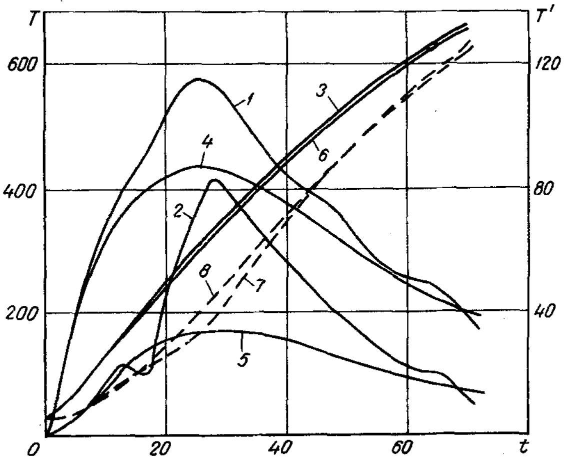

Fig. 3. Temperature curves derived on the experimental installation and used for the calculations based on formulas (2), (3), and (4): 1) ΔT_{1t}; 2) ΔT_{2t}; 3) T_{1t}; 4) ΔT_{1s}; 5) ΔT_{2s}; 6) T_{1s}; 7 and 8) average temperatures for the coal load (T_t) and for the standard material (T_s), calculated according to formula (2). The 600-degree scale corresponds to the curves for T_{1t}, T_{1s}, T_t, and T_s. The scale for the duration of the heating is given in min.

The piston is made of a high-melting glass which is a comparatively poor conductor of heat and which is fabricated with orifices to transmit the gaseous products which are formed during the heating process. To ensure identity of conditions, the beaker containing the standard substance is fitted out with a similar piston.

The distribution of the thermocouples is shown in Figs. 1 and 2. Each of the containers [cells]—housing three thermocouples each—give recordings of three emf's which correspond to the temperatures

$$T_{1t} - T_{2t} = \Delta T_{1t},\quad T_{2t} - T_{3t} = \Delta T_{2t},\ T_{1t},$$
$$T_{1s} - T_{2s} = \Delta T_{1s},\quad T_{2s} - T_{3s} = \Delta T_{2s} \text{ and } T_{1s}$$

(the subscripts "t" and "s" denote that the thermocouples pertain, respectively, to the cell with the test coal load and the standard material).

A conventional EPP-09 automatic potentiometer with a scale ranging to 600° C was employed for recording purposes. Its bridge circuit was modified by the method proposed in [6], as a result of which it became possible to record the temperatures ΔT_{1t}, ΔT_{2t}, ΔT_{1s} and ΔT_{2s} directly (the scale of the device in this case corresponded to 120° C). To record the temperatures T_{1t} and T_{1s} by means of which the average temperatures are calculated for the loads of the test and standard materials, the thermocouples are automatically shunted at the appropriate instants of time so that their readings correspond to a 600-degree scale.

During the course of the experiment, the current supplied to the heater spiral is not regulated, i.e., the rise in the temperatures T_{1t} and T_{1s} is not kept linear.

However, if the heating regime were strictly linear, and the thermal indices of the diathermic shell and the substances being heated were not changing with a rise in the temperature, the differences between the temperatures ΔT_{1t}, ΔT_{2t} and ΔT_{1s}, ΔT_{2s} with the passage of time would tend toward a specific limit, subsequently remaining constant, and this would correspond to the establishment of a quasi-steady regime. The form of this function—exponential [7]—is quite familiar in numerous physical phenomena and is expressed, for example, in the case of ΔT_{1s}, by a formula derived under the condition that the law governing the change in temperature at the outside surface of the diathermic shell and the heat flow expended on the heating of the materials contained within the shell are specified:

$$\Delta T_{1s} = \frac{(c_0 m_0 + c'_s m'_s)\, n \ln\left(\frac{d_2}{d_1}\right)}{2\pi L \lambda_0} \times \left\{1 - \exp\left[\frac{2\pi L \lambda_0 t}{(0.4\, c_0 m_0 + 1.4\, c'_s m'_s)\ln\left(\frac{d_2}{d_1}\right)}\right]\right\}. \quad (1)$$

If we take into consideration the change (an increase, in our case) in the coefficient of thermal conductivity for the shell during the heating process and if we consider the nonlinearity of the change in time for the surface temperature of the shell, the curve must change its exponential character and develop an extremum with a clearly defined maximum. The curves corresponding to the test material—for which the laws governing the variations in heat capacity and thermal conductivity may be random in character—are more complex in form. The experimental curves which have been derived correspond to these considerations.

Figure 3 shows the curves corresponding to the heating of pulverized Tkibuli coal (with the following mesh-size distribution in m · 10^{-6} : 200–250) 9%; 200–150) 21%; 150–100) 30%; 100–50) 24%; < 50) 16%) with a moisture content of 6%; the standard material is a powdered aluminum oxide that is usually employed in thermography as the standard for work with coal.

The nature of the resulting curves $\Delta T_{1t} = f_1(t)$ and $\Delta T_{2t} = f_2(t)$ corresponds to the phenomena occurring in the charging of coal in heating: the phenomenon of heat and moisture conductivity at 80–100° C; the evaporation associated with the unbound moisture at 100–160° C; and the exothermic (at 340–360 and 460–500° C) and endothermic (at 390–430 and 550–580° C) effects.

From the six derived curves we can calculate the average temperatures for the test and standard materials, and then the thermal characteristics of the coal load of interest to us, provided that we know the temperature relationships for the coefficient of thermal conductivity and the heat capacity of the standard material.

Considering the fact that the load is shaped in the form of a hollow cylinder and that the temperature distribution within this cylinder is nearly parabolic [8], the average temperature of the standard material is expressed by the formula

$$T_s = T_{1s} - \Delta T_{1s} - 0.4\,\Delta T_{2s}. \tag{2}$$

Analogous formulas are used to determine the average temperature for the test material and the average temperatures used in the derivation of formula (1). The dashed lines in Fig. 3 show the change in the average temperatures of the coal and standard layers, corresponding to the solid curves of that figure.

The change in the thickness of the material layer alters the accuracy with which the temperature is determined. Thus, the temperature of a layer of minimum thickness simultaneously reflects the average and true temperature. With an increase in the thickness of the layer, the inaccuracy in the determinatinn of the average temperature will increase. Having chosen a specific layer thickness, we proceed on the assumption that the processes of heat transfer in an actual load cannot be modeled [simulated] in a layer of minimum thickness, since the processes occurring in the adjacent layers (both on the hot and cold sides) affect the processes of heat and mass transfer in a small layer of finite dimensions. For each type of test material it is therefore possible to arrive at a theoretically valid minimum possible layer thickness which will yield an adequate approximation of the conditions needed to perform industrial operations (in our case, as noted above, this thickness is equal to 8 mm). On the basis of the selected layer thickness, it becomes possible to alter other geometric characteristics of the cell as well.

To find the values of the heat capacity for a specific temperature, we propose a simple formula which is structurally similar to the formula offered by Berg and Yagfarov:

$$c_t = c_s \frac{m_s}{m_t} \frac{\Delta T_{1t}}{\Delta T_{1s}}\bigg|_{T_s=T_t}. \tag{3}$$

The values of c_s and ΔT_{1s} are taken for the average temperature of the standard material, which is equal to the average temperature of the test material. Indeed, given equal average temperatures for the two layers, the readings of the differential thermocouples (ΔT_{1t} and ΔT_{1s}) will be proportional to the quantities of heat received by the standard and test materials in an infinitely small interval of time. Thus, the value of the heat capacity derived from formula (3) expresses the effective value of the heat capacity for a specific temperature.

The change in the coefficient of thermal conductivity as a function of temperature is also defined by the relative method on the basis of the familiar relationship for the change in the coefficient of thermal conductivity for the standard material. The formula used in this case is the following:

$$\lambda_t = \lambda_s \frac{\Delta T_{2s}}{\Delta T_{2t}} \frac{\Delta T_{1s}}{\Delta T_{1t}}\bigg|_{T_s=T_t}. \tag{4}$$

The resulting value will express the effective value of the coefficient of thermal conductivity for a specific temperature. Indeed, the coefficients of thermal conductivity for the substances in the two cells are inversely proportional to the differences between the temperatures ΔT_{2s} and ΔT_{2t} when the quantities of heat supplied in both cases are kept constant. The coefficient $\Delta T_{1s}/\Delta T_{1t}$ enables us to account for the existing inequality in the quantities of heat supplied. It is introduced in the assumption that the relationship between the magnitude of the heat flux and the temperatures ΔT_{2s} and ΔT_{2t} is directly proportional, all other conditions being equal.

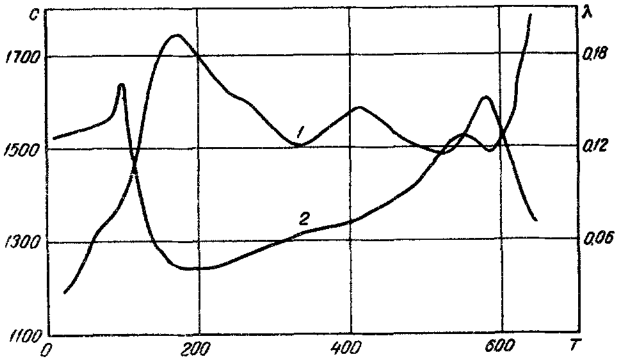

Fig. 4. Temperature relationships for the heat capacity c, in J/kg · deg (1) and the coefficient of thermal conductivity λ, in W/m · deg (2) for a load of Tkibuli coal ($W^a = 6.0\,\%$; $A^s = 14.10\,\%$; $V^g = 39.75\,\%$).

The coefficient of thermal conductivity is calculated from the familiar formula

$$a = \frac{\lambda}{c\rho}. \tag{5}$$

The imperfect nature of the method by which the heat flow is supplied to the cells and by which the heat flow itself is measured, as well as the above-indicated assumptions, introduce no significant distortions into the results that are obtained, since the latter are offset by the relative nature of the measurements in the proposed method.

Formulas (3), (4), and (5) were used to calculate the temperature relationships of the thermal constants for the loads of the Tkibuli coal (prepared in a variety of ways), and for the coke made from this coal; these relationships showed that reproducible results are possible by this method. The reproducibility of the various effects—the total and absolute magnitude of the ordinates of the curves, corresponding to the repeated experiments—did not differ, one from the other, by more than 3.0%.

Figure 4 shows the functions $\lambda = f_1(T)$ and $c = f_2(T)$ for a load of Tkibuli coal, corresponding to the curves in Fig. 3.

The specific heat of the aluminum oxide was taken from the following formula [9]:

$$c_p = (1005 + 0.29T)\ \text{J/kg} \cdot \text{deg}$$

The coefficient of thermal conductivity as a function of the temperature of the powdered aluminum oxide (particle diameter 15–20 · 10^{-6} m; ρ = 1000 kg/cm^3; load porosity, 72%) was taken from literature data [1,10, 11]:

Temperature, °C	0	100	200	300	400	500	600
λ, $\frac{\text{W}}{\text{m} \cdot \text{deg}}$	0.139	0.135	0.132	0.134	0.138	0.147	0.158

The resulting values for the thermal characteristics are in agreement with the few literature data characterizing the effective values of the thermal constants for coals [5,12]. The values of the integral heats expended on the heating of the coal load to a specific temperature (calculated from the $c = f(T)$ curves) are in agreement with the Pieper [13] calorimetry experiments.

NOTATION

c_0, m_0, c_s, m_s, c_t, and m_t are the specific heat capacities and masses of the diathermic shell, and of the standard and test materials; c_s' and $m_s' = \Sigma c_n m_n$, c_n, and m_n are the specific heat capacities and masses of the materials inside the diathermic shell (a beaker, the actual material, and a center rod); d_1, d_2, and L are the inside and outside diameters and the height of the diathermic shell; λ_0, λ_s, and λ_t are the thermal conductivities of the diathermic shell, the standard and the test materials; t is the heating time; $n = T_{1s}/t$ is the coefficient of temperature-rise linearity; T_s and T_t are the average temperatures for the loads of standard and test materials; ρ is the density; a is the thermal diffusivity; W^a, A^s, and V^g are conventional notations for the technical properties of coal.

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