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APPLICATION OF A STRUCTURAL MODEL TO THE ELUCIDATION OF THERMAL CHARACTERISTICS OF DISPERSIVE SUBSTANCES

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In a theoretical way the author suggests a solution of the effect of humidity on the heat parameters of dispersive substances with regard to the crude masses of technical porcelain. He idealizes the structure of these materials in a structural model, the basis of which are spherical grains containing microscopic pores. On the basis of these concepts he determines the quantitative dependence of the heat quantities of the dispersive substance on humidity. Theoretical conclusions applied to technical porcealin are in good agreement with empirical results.

I. INTRODUCTION

In the physic of dispersive materials we try to obtain the qualitative and quantitative analysis of the process of heat transfer through the medium of the structural model of the substance. On the basis of the known reological and technological properties of the crude materials of the technical porcelain we have set up its structural model. In a theoretical way we have stated the effect of humidity on the specific thermal conductivity, the specific thermal capacity and the heat conductivity of crude electroporcelain. These theoretical conclusions have been confirmed in the experimental part of our research. Contrary to the supplement of the czechoslovak Standard (ČSN 128001) we understand under the term the weight proportion of humidity in a substance (in short „the weight humidity“) the relative number, which is given by the proportion of the weight of water in a substance to the total weight of the substance. Thus defined weight humidity will be designated by the symbol w. The above change is substantiated by its usefulness in theoretical reflections regarding the structural model. The proportion of the volume of water in a substance and of the total volume of the substance will be called the volume proportion of humidity in the substance (in short volume humidity)and will be designated by w_0.

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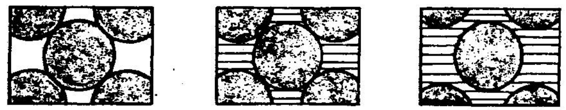
II. THE STRUCTRURAL MODEL OF THE CRUDE MASS OF ELECTROPORCELAIN

Technical porcelain belongs to the group of hard porcelain containing 50 % kaolin, 25 % quartz and 25 % feldspar. In the phase of the preparation of the crude masses the basic raw materials are ground into grains averageing less than 10 μm. In this respect technical porcelain belongs to the group of fine-grain dispersive materials [1, 2]. In the subsequent technological processing the originally vacuumized mass, the initial humidity of which is $w \doteq 0.30$, is gradually completely desiccated.

Starting from the knowledge of the theoretical properties and technological processing of porcelain we can state that in best agreement with reality is that model, in which the basic substance (the skeleton) has the shape of spheric grains with microscopic capillary pores. The remaining part of the space is free of air and thus contains only the liquid phase, i. e. water. The process of desiccation is first brought about by the evaporation of water from the intergrain spaces (Fig. 2), the substance contracts and the grains get nearer to each other. This process continues till the grains touch, which is in correspondence to the arrangement of grains in a simple cubic structure (Fig. 3). By further desiccation the arrangement becomes a tetragonal, spa-



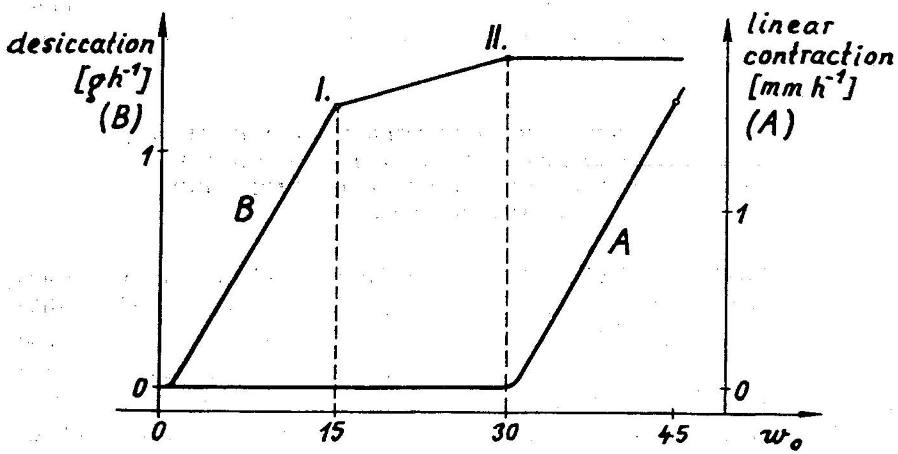


Fig. 1. Linear contraction A and desiccation velocity B of raw electroporcelain dependent on humidity.

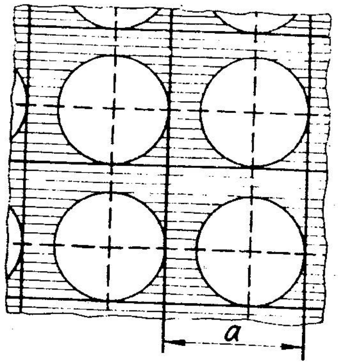


Fig. 2.

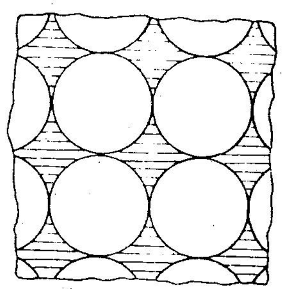


Fig. 3.

tially centred arrangement [3]. In this arrangement the contraction is completed, the grains get close to each other, the desiccation continues starting in the integrain spaces and finally in the grains proper. This idea of the contraction and of the desiccation speed is in agreement with reality, since we have measured the shrinkage of material up to the weight humidity of $w = 0.18$, which corresponds to the moment of the contact of grains in the tetragonal arrangement (volume humidity $w_0 = 0.30-0.35$). The process of desiccation with marked individual stages of humidity release is illustrated in Fig. 1. Curve A represents the linear contraction, curve B the speed of desiccation of the sample. On the abscissa the volume humidity w_0 is plotted which is determining for the general model. The breaks on line B correspond to the lowering of the evaporation speed during the transition to the closest arrangement (II.) and to the moment of the beginning of the release of capillary humidity (I.).

III. DEPENDENCE OF SPECIFIC THERMAL CONDUCTIVITY, SPECIFIC THERMAL CAPACITY AND HEAT CONDUCTIVITY ON HUMIDITY AS DETERMINED FROM THE MODEL OF THE SUBSTANCE

In the following we shall use these symbols: r — radius of spheric grains, λ_1 — specific thermal conductivity of grains filled with capillary humidity, λ_0 — specific thermal conductivity of completely desiccated grains, λ_2 — specific thermal conductivity of water, λ_3 — specific thermal conductivity of air, C_s — specific thermal capacity od completely desiccated grains, C_t — specific thermal capacity of water, C_3 — specific thermal capacity of air, ϱ_1 — specific gravity of grains filled with capillary water, ϱ_2 — specific gravity of water, ϱ_3 — specific gravity of air.

Further we denote the resulting specific thermal conductivity by λ, the specific thermal capacity by C, the heat conductivity by k. The intervals of humidity will be denoted by the parameters of humidity, which will be introduced in the latter part of the paper and at the same time by the weight humidity w, calculated for the masses of technical porcelain No 13.

1. Specific thermal conductivity

In view of the geometrical distribution of the basic phases of the substance in the process of desiccation we have to divide the solution of this problem into four parts (a—d).

a. We determine the thermal conductivity of the system at its transition from the state in which every grain occupies a cubic space with a side equal to $a(a \geqslant 2r)$, filed with water (Fig. 2), up to the contact of grains in the cubic arrangement (Fig. 3).

Humidity is determined by the parameter r/a. The minimum humidity in this interval corresponds to the value $r/a = \frac{1}{2}$, when the volume of grains is $p_1 = 0.5237$ and the water content outside the grains is $p_2 = 1 - p_1 = 0.4763$ of the total volume of the sample.

The thermal resistance R_0 of the basic configuration, i.e. of a cube with an edge equal to $2r$, within which there is the spheric grain with the radius r and the remaining space is filled with water (Fig. 4), is

$$R_0 = \frac{\ln \dfrac{[\pi(\lambda_1 - \lambda_2) + 4\lambda_2]^{1/2} + [\pi(\lambda_1 - \lambda_2)]^{1/2}}{[\pi(\lambda_1 - \lambda_2) + 4\lambda_2]^{1/2} - [\pi(\lambda_1 - \lambda_3)]^{1/2}}}{r\{[\pi(\lambda_1 - \lambda_2) + 4\lambda_2]\, \pi(\lambda_1 - \lambda_2)\}^{1/2}} . \qquad (1)$$

Equation (1) under the assumption that

$$\left[\frac{\pi(\lambda_1 - \lambda_2)}{\pi(\lambda_1 - \lambda_2) + 4\lambda_2}\right] < 1$$

can be written in the simple form of

$$R_0 = \frac{2}{r[\pi(\lambda_1 - \lambda_2) + 4\lambda_2]} . \qquad (2)$$

The specific thermal conductivity λ' of the configuration in Fig. 4 is

$$\lambda' = \frac{\pi(\lambda_1 - \lambda_2)}{4} + \lambda_2 .$$

The relation (2) is applied to the calculation of the specific thermal conductivity of the arrangement in Fig. 2 at the ratio of $r/a < \frac{1}{2}$. The basic configuration

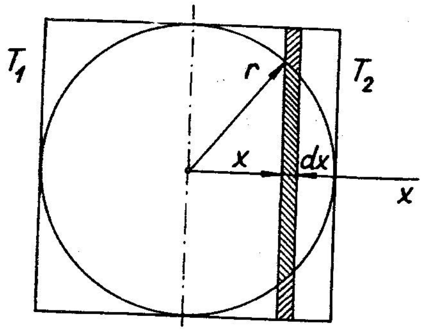


Fig. 4.

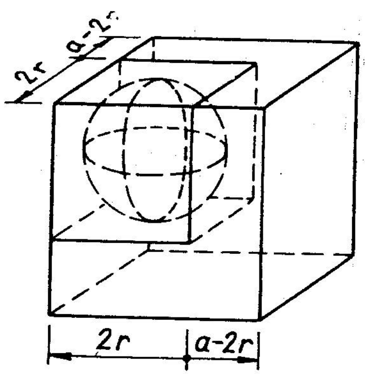


Fig. 5.

from which we start the calculation, can be seen in Fig. 5. The thermal conductivity of this configuration is not dependent on the position of the grain in it. We assume that heat transfer occurs between two opposite faces; the heat leakage through the lateral faces is neglected. The thermal conductivity of the whole configuration is

$$G = G_1 + \lambda_2 \frac{a^2 - 4r^2}{a}, \tag{3}$$

where G_1 is the thermal conductivity of a zone of the quadratic prism with the length a and the cross-section $4r^2$, in which the grain is situated. The resistance of this zone is

$$R_1 = \frac{1}{G_1} = R_0 + \frac{a - 2r}{4r^2 \lambda_2}. \tag{4}$$

By means of (2) and (4) the relation (3) can be written in the form

$$G = \lambda_2 \frac{a^2 - 4r^2}{a} + \frac{4r^2\lambda_2[\pi(\lambda_1 - \lambda_2) + 4\lambda_2]}{\pi(\lambda_1 - \lambda_2)(a - 2r) + 4\lambda_2 a} \tag{5}$$

and from this equation we have for the specific thermal conductivity

$$\lambda = \lambda_2 \left[1 - \left(2\frac{r}{a}\right)^2\right] + \frac{\lambda_2 \left(2\frac{r}{a}\right)^2 [\pi(\lambda_1 - \lambda_2) + 4\lambda_2]}{(\lambda_1 - \lambda_2)\left(1 - 2\frac{r}{a}\right) + 4\lambda_2}. \tag{6}$$

The parameter r/a is the humidity factor and we can express it by the weight

humidity w. If p_0 is the weight proportion of water contained in the grains, then the following holds

$$\frac{r}{a} = \left\{\frac{3\varrho_2(1 - w)}{4\pi[\varrho_1(w - p_0) + \varrho_2(1 - w)]}\right\}^{1/3}. \tag{7}$$

Relations (6) and (7) hold true for the humidity interval $0 \leqslant r/a \leqslant \frac{1}{2}$, which for electroporcelain masses corresponds to the interval of the weight humidities $1.00 \geqslant w \geqslant 0.31$.

b. At the transition of grains into the closest arrangement there occur an approximation of eight grains (four from the top, four from the bottom) towards the grain that we have chosen in the elementary cell as basic. In the closest arrangement the basic grain gets in touch with the 12 neighbouring ones. The basic cell in its diagonal cut has the shape as shown in Fig. 6. The dimensions of the basic cell change by desiccation. With a humidity of $w = 0.31$ it has a height of $4r$ (illustrated in Fig. 6 with a solid line), with the closest arrangement only $2r\sqrt{2}$, illustrated with a dash and dot line. In the general position the centres of the group of four grains in the corners of the basic cell are at the distance z from the plane that limits the basic grain from the top and the bottom respectively. This position of the grains is illustrated in Fig. 6 by a dash line. The ratio z/r is the factor of humidity.

With respect to the geometrical arrangement of the basic phases we have to determine separately the thermal resistance of the layers I—III. The total resistance of the cell is

$$R = R_{\mathrm{I}} + R_{\mathrm{II}} + R_{\mathrm{III}} = \frac{r + z}{\lambda 4r^2}.$$

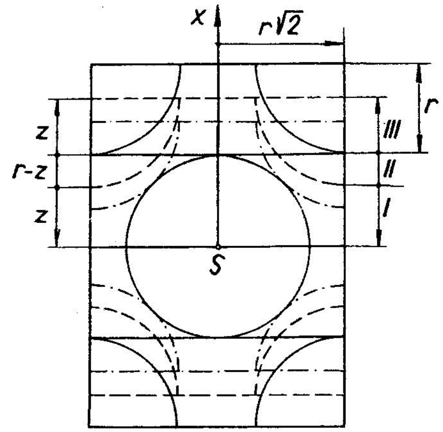


Fig. 6.

Then the specific thermal conductivity is given in the equation

$$\lambda = \frac{r + z}{4r^2(R_{\mathrm{I}} + R_{\mathrm{II}} + R_{\mathrm{III}})} . \tag{8}$$

The resistances R_i are determined by means of the integrals of the type

$$R_i = \int_{x_1}^{x_2} \frac{\mathrm{d}x}{\lambda_1 S_1(x) + \lambda_2 S_2(x)} = \int_{x_1}^{x_2} \frac{\mathrm{d}x}{Ax^2 + 2Bx + C} ,$$

($S_1(x)$ is the solid part and $S_2(x)$ the liquid part of the whole cross-section of the cell). Their solution for $B^2 > AC$ is

$$R_i = \frac{1}{2a} \ln \frac{d - B - Ax}{d + B + Ax} ,$$

where $d = (B^2 - AC)^{1/2}$.

For the sake of an easy survey of the procedure we give the basic data of the integrals R_i in Table 1 and Table 2.

Table 1

Layer	Integration limits	$S_1(x)$	$S_2(x)$
I	$r \leqslant x \leqslant z$	$\pi(r^2 - x^2)$	$4r^2 - (r^2 - x^2)$
II	$z \leqslant x \leqslant r$	$\pi[2r^2 - (r+z-x)^2 - x^2]$	$4r^2 - \pi[2r^2 - (r + z - x)^2 - x^2]$
II	$z \leqslant x \leqslant r$	$\pi[r^2 - (r+z-x)^2$	$4r^2 - \pi[r^2 - (r + z - x)^2]$

Table 2

Layer	A	B	C
I	$-\pi(\lambda_1 - \lambda_2)$	0	$r^2[\pi(\lambda_1 - \lambda_2) + 4\lambda_2]$
II	$-2\pi(\lambda_1 - \lambda_2)$	$\pi(\lambda_1 - \lambda_2)(r + z)$	$\pi(\lambda_1 - \lambda_2)[2r^2 - (r + z)^2] + 4r^2\lambda_2$
III	$-\pi(\lambda_1 - \lambda_2)$	$\pi(\lambda_1 - \lambda_2)(r + z)$	$\pi(\lambda_1 - \lambda_2)[r^2 - (r + z)^2] + 4r^2\lambda_2$

The resistances R_{I}, R_{II}, R_{III} are after some simplifications given by the equations

$$R_{\mathrm{I}} = \frac{1}{r} \frac{z/r}{\pi(\lambda_1 - \lambda_2) + 4\lambda_2} , \tag{9}$$

$$R_{\mathrm{II}} = \frac{1 - \frac{z}{r}}{\pi r(\lambda_1 - \lambda_2)\, d_0^2} \tag{10}$$

$$d_0 = \left\{4\left[1 + \frac{2\lambda_2}{(\lambda_1 - \lambda_2)}\right] - \left(1 + \frac{z}{r}\right)^2\right\}^{1/2} , \tag{11}$$

and

$$R_{\mathrm{III}} = R_{\mathrm{I}} .$$

It follows from equations (10)—(13) that

$$\lambda = \frac{1 + z/r}{\frac{z}{r} \frac{8}{4\lambda_2 + \pi(\lambda_1 - \lambda_2)} + \frac{4}{\pi(\lambda_1 - \lambda_2)} \frac{1 - (z/r)}{d_0^2}} . \tag{12}$$

For the relation of the parameter z/r and the weight humidity there holds

$$\frac{z}{r} = \frac{(\pi - 3)(1 - w)\,\varrho_2 + \pi\varrho_1(w - p_0)}{3\varrho_2(1 - w)} .$$

The extreme weight humidities which correspond to the interval $0.41 \leqslant z/r \leqslant 1.00$ are for the masses of technical porcelain $w = 0.18$ and $w = 0.31$.

c. The determination of specific thermal conductivity in the interval of humidities from $w = 0.18$ to the release of the inter-grain water presupposes the knowledge of the water distribution in the neighbourhood of the grains. The determination of the cross-section $S_2(x)$ of water at the distance x from the centre of the cell is rather complicated. Any relations set up for this quantity cannot be much relied upon. Therefore in this interval we confine ourselves to only the determination of the specific thermal conductivity at the extreme points of the humidity interval. The specific thermal conductivity for $w = 0.18$ will be determined from the model (b), where $z/r = 0.41$ By the decrease of humidity to the value $w = 0.07$ there occurs a complete evaporation of water from the inter-grain spaces and the remaining water is contained in the grains capillaries. The specific thermal conductivity for $w = 0.07$ is determined from the relation (12), where we substitute $z/r = 0.41$ and instead of λ_2 we write in the equation λ_3, i.e. the specific thermal conductivity of air.

d. The specific thermal conductivity in the interval of weight humidities below 0.07 cannot be determined by the method of the structural model. It is clear that the specific conductivity of the cell with the humidities $w = 0.07$ and $w = 0.00$ is approximately equal to the thermal conductivity of the grains of the material saturated completely with water and completely desiccated. Both these parameters must be known for the solution of the structural model and we obtain them in experimentally.

2. Specific thermal capacity

From the structural model and the considerations mentioned in 1, there follow for the specific thermal conductivity these relations

$$C = C_2 - (C_2 - C_t)\frac{4\pi}{3}\left(\frac{r}{a}\right)^3, \quad \text{for } w > 0.31 \tag{14}$$

$$C = C_2 - (C_2 - C_t)\frac{\pi}{3\left(\frac{z}{r}+1\right)}, \quad \text{for } 0.18 \leqslant w \leqslant 0.31 \tag{15}$$

$$C_7 = C_s + \frac{\pi \varrho_1 c_2 p_0}{4.24}, \quad \text{for } w = 0.07 \tag{16}$$

$$C_0 = C_s \text{ (dry material)}, \quad \text{for } w = 0.00 \tag{17}$$

C_0 is the quantity determined experimentally. The parameters r/a and z/r, respectively, required in equations (12), (13) are determined for the humidity in question for equations (7) and (13).

3. Heat conductivity

The heat conductivity is determined from its definition

$$k = \lambda / C.$$

IV. FORMULATION OF THERMAL CHARACTERISTICS FOR THE ELECTROPORCELAIN CRUDE MASS No 13

We determined the specific thermal conductivity and the specific thermal capacity in part III as the function of suitably chosen parameters r/a and z/r, respectively, which we expressed by means of the weight humidity ((7), (13)). For the sake of an easy survey of the explanation we used at the same time true values of the weight humidity of the electroporcelain crude mass, starting from its known parameters that will be given later.

By measuring we have found the following parameters of the mass No 13: $\varrho_1 = 2.628$ gcm^{-3}, $\lambda_0 = 0.468$ Wm^{-1}deg^{-1}, $\lambda_1 = 1.409$ Wm^{-1}deg^{-1}, $C_s = 1.801$ Jcm^{-3}deg^{-1}. In addition to these quantities we have used the parameter of water and air [4].

Relations (12), (15) and (13) are then simplified into the form

$$\lambda = \frac{1 + z/r}{1.618\frac{z}{r} + \frac{1.568(1 - z/r)}{5.876 - (1 + z/r)^2}} \quad [\text{Wm}^{-1}\text{deg}^{-1}]$$

$$C = 4.178 - \frac{1.685}{1 + z/r} \; [\text{J cm}^{-3}\text{deg}^{-1}],$$

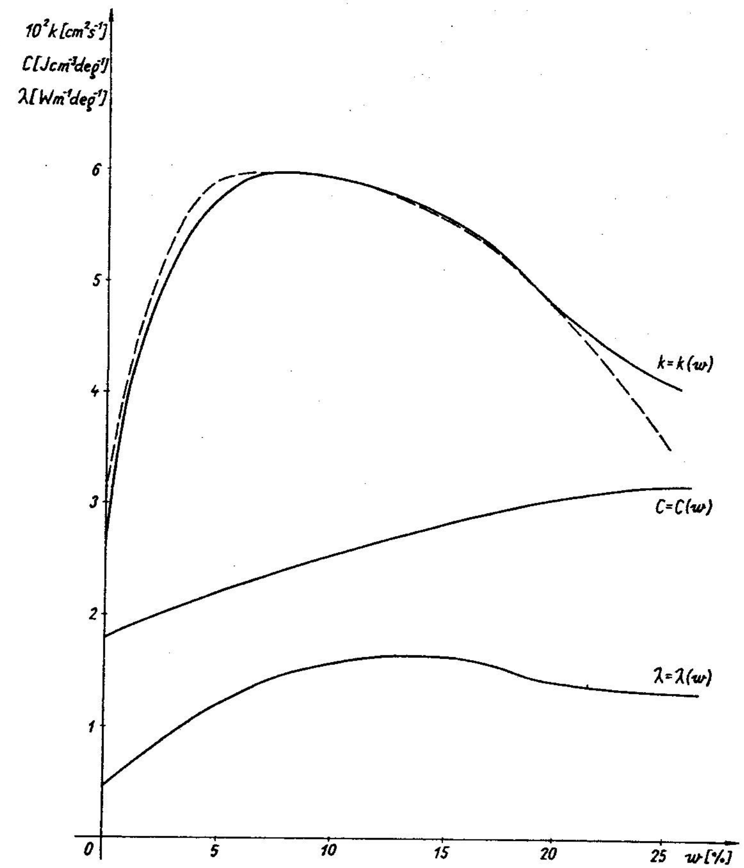


Fig. 7. Dependences $\lambda = \lambda(w)$, $C = C(w)$ and $k = k(w)$ obtained by means of the structural model (in full line). Dependence $k = k(w)$ found experimentally is given in dotted line.

$$w = \frac{0.14 + z/r}{2.71 + z/r} \qquad [1].$$

From the structural model we get the characteristics $\lambda = \lambda(w)$, $C = C(w)$ and $k = k(w)$, illustrated in Fig. 7. In Fig. 7. we have shown by a dashed line the dependence $k = k(w)$ obtained by measuring.

V. CONCLUSIONS

From the comparison of the characteristics $k = k(w)$, obtained in a theoretical and experimental way, we can see that the structural model describes in a sufficiently exact manner the true process of desiccation of the dispersive substance. This agreement is significant, especially in the range of the weight humidity 0.07—0.25. In spite of the fact that in the construction of the structural model and its analysis we made many approximations for the sake of a better solution of the problem, the model is a sufficiently exact description of the real state and facilitates the qualitative explanation and quantitative of the phenomena occurring at the desiccation of some grainy dispersive material.

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