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THE EXPERIMENTAL INVESTIGATION OF HEAT AND MASS TRANSFER IN THE PRESENCE OF CHEMICAL CONVERSIONS

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Abstract—The results of the experimental investigations on heat and mass transfer in the process of kilning the kaolin and the magnesium hydroxide are adduced in this paper. An experimental installation was developed which allows the temperature field of the heated body, its mass loss and the thermophysical characteristics of the body to be determined. The thermal conductivity coefficients and the coefficients of thermal diffusivity, heat capacity and the heat transfer coefficient of the mentioned substances were defined in the temperature range from 200° to 1000°C. It was found that the chemical conversions begin at the surface of the capillary porous body and then spread gradually into the interior of the body. The chemical conversion zone deepens into the body according to the parabolic law.

Résumé—Cet article apporte de nouveaux résultats quant aux recherches expérimentales sur la transport de chaleur et de masse dans le mécanisme de la cuisson du kaolin et de l'hydroxide de magnésium. Une installation a été construite pour mesurer le champ des températures dans le corps chauffé, la perte de masse et les caractéristiques thermiques. Les coefficients de conductibilité thermique, de diffusivité thermique, la capacité calorifique et le coefficient de transmission de chaleur des substances ci-dessus ont été étudiées entre 200 et 1000°C. On a trouvé que les réactions chimiques commencent à la surface du corps poreux et s'étendent graduellement dans l'intérieur du corps. La réaction chimique se développe à l'intérieur du corps suivant une loi parabolique.

Zusammenfassung—Diese Arbeit behandelt den Wärme- und Stofftransport beim Brennen von Kaolin und Magnesiumhydroxyd. In einer Versuchapparatur konnten das Temperaturfeld des geheizten Körpers, sein Massenverlust und seine thermischen Stoffwerte bestimmt werden. Die Wärmeleitfähigkeit, die Temperaturleitfähigkeit, die Wärmekapazität und der Wärmeübergangskoeffizient der genannten Substanzen wurden im Temperaturbereich von 200 bis 1000°C gemessen. Man fand, dass die chemische Reaktion an der Oberfläche des kapillarporösen Körpers begann und sich nach einem Parabelgesetz in das Innere fortpflanzte.

Аннотация—В статье приведены результаты экспериментальных исследований по тепло-и массообмену в процессе обжига каолина и гидроокиси магния. Разработана экспериментальная установка, позволяющая регистрировать температурное поле нагреваемого тела и его массоотдачу, а также определять теплофизические характеристики тела.

Определены коэффициенты теплопроводности и температуропроводности, теплоёмкость, коэффициент теплообмена указанных материалов в интервале температур от 200°C до 1000°C.

Установлено, что химические превращения начинаются на поверхности капиллярно-пористого тела, а затем постепенно перемещаются внутрь тела. Зона химических превращений углубляется внутрь тела по закону параболы.

THE present paper deals with the investigation of heat and mass transfer in capillary porous bodies in the presence of chemical conversions. These processes take place more clearly during the kilning of ceramic ware and also of kaolin kilning.

Thermal effects of a different nature become apparent in a certain temperature range when the majority of mineral substances are heated. These phenomena occurring during heating of the mineral substances are described qualitatively by means of the heating–kinetics curves.

An experimental laboratory installation shown in Fig. 1 has been developed to study the kinetics of the process of the kilning of mineral substances. This installation consists of two electric crucible furnaces of the same type (1 and 2). The cast-iron sleeve-bearings were inserted into the furnace to maintain level temperatures along its height.

A sample of the investigated substance made in the form of a plate or a cylinder was put into one of the furnaces. Three thermocouples were inserted into the sample to measure the temperature drop at various points of it. The temperature drop between the surrounding medium and the surface of the sample was measured by thermocouple (1) (Figs. 1 and 2). Thermocouple (2) shows the difference between the surface temperature and the temperature at the point $x = R/2$ where R is half the plate thickness or the cylinder radius. Thermocouple (3) shows the difference between the surface temperature and the temperature at the centre of the sample (plate or cylinder). The butt ends of the cylindrical sample are covered with the heat-insulating seal made out of burned asbestos thus making it possible to consider the sample as an unlimited cylinder for the purpose of calculation.

An analogous sample suspended on an automatic self-recording balance was kilned in the second furnace (Fig. 1) in order to record the curve of mass-transfer kinetics. The air temperature in the furnaces increased linearly with time (the heating velocity remained constant). This was ensured by the electronic regulator (5) with the command apparatus (see Fig. 1). The resistance boxes (3) and (4) with the galvanic elements served both for zero creep when recording the temperature and for increasing the sensitivity of the self-recording potentiometer.

The specially designed automatic self-recording balance was applied for receiving the weight-drop curve (mass transfer) of the investigated

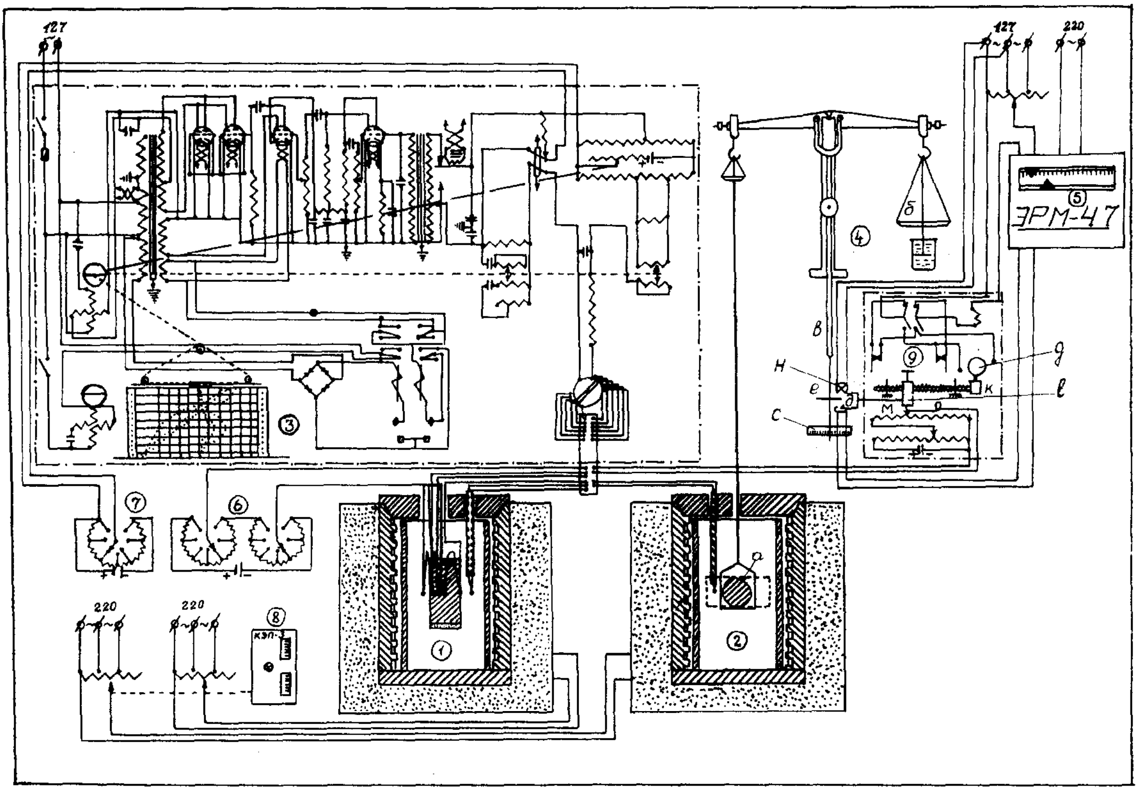

FIG. 1. The scheme of the experimental installation for the record of the curves of the heating process kinetics of the capillary porous bodies.

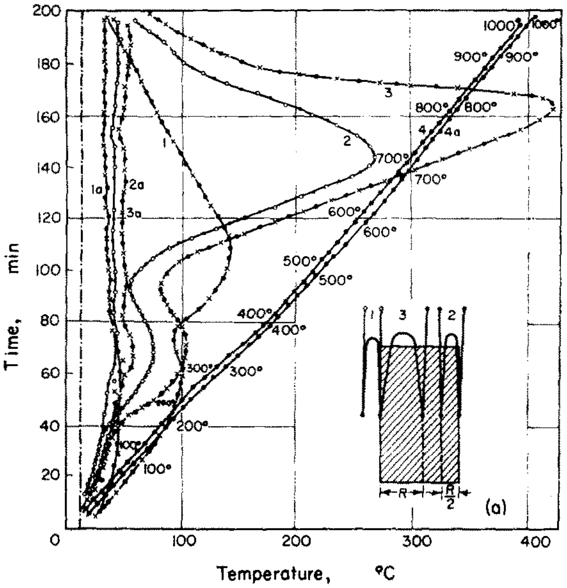

FIG. 2. The heating curves in the process of kilning the cylinder made out of the magnesium hydroxide.

sample. The investigated sample (*a*) may be suspended from the left scale, and by the weight (δ) it is balanced in such a way that the pointer (*b*) has to be placed at the left side of the scale (*c*) and the movable carriage (*e*) has to be at the extreme left position. With the decrease in the sample weight the pointer (*b*) deviates to the left and a screen gate (*e*) attached to the pointer moves together with it thus opening the chink above the photoelectric cell. When the chink is opened the ray from the lighting apparatus (*H*) illuminates the photoelectric cell. The photoelectric current reaches the millivoltmeter of the electronic governor (5), which switches on the electromotor (*g*) through the reductor (*k*) and moves the carriage (*l*) till the screen gate covers the ray from the lighting apparatus. Then the circuit is broken and the carriage stops moving. The photoelectric cell, the lighting apparatus and the slide of the rheostat are mounted on the moving carriage. When the slide moves along the rheostat (*M*) the taken-off voltage changes and comes in the sockets of the automatic multipoint potentiometer. The change of the taken-off voltage from the rheostat is proportional to the shift of the pointer (*c*) and the self-recording potentiometer records a curve which corresponds to the decrease in the weight of the investigated sample. The total weight loss of the sample for the whole kilning process is determined either by making the pointer return to its initial position with the help of a weight, or by weighing the kilned sample after it has been cooled in an desiccator. The rise of the endothermic thermal effect (the heat absorption caused by chemical reactions) at the surface of the sample when the corresponding furnace temperature is obtained is marked on the curves for the sample heating. Thermocouple (1) will show the increase of temperature drop since its hot junction placed at the cylinder surface marks the lag in the surface temperature increase caused by the endothermic effect. At this instant thermocouples (2) and (3) register some decrease in temperature difference between the surface of the sample and the points inside the sample at $x = 0$ and $x = R/2$. The chemical conversions accompanied by the endothermic effect occur at first only at the surface of the sample and not in the whole volume of it. After the termination of the chemical conversions at the surface of the sample the chemical reaction zone will gradually occur deeper in the sample centre. Thermocouple (1) will show then the decrease in temperature drop, while thermocouples (2) and (3) show the increase in it. This drop occurs due to the fact that the temperature at the surface of the sample is continuously rising while the temperature in the deep parts of the sample will be rising more slowly, since the heat entering the sample will be partially absorbed in the region of chemical conversions.

The transition of the point $x = R/2$ where the thermocouple (2) is placed by the deepening front of the endothermic reaction zone is registered on the curve of heating kinetics by abrupt decrease in temperature drop for this sample layer. At the same time thermocouple (3) will continue to show the increase in temperature drop till the endothermic reaction zone reaches the sample centre.

The exothermal effects (chemical conversions, connected with heat evolution) arising in the regions of the thermocouples in the sample are registered in the same way by bends and gaps on the heating kinetics curves.

Synthetic magnesium hydroxide and kaolin (the Dubrovo deposits) were used for our investigations as mineral substances.

The typical heating kinetics curves in the kilning process are given in Fig. 2 for one of the experiments. The experimental sample is made from synthetic magnesium hydroxide in a form of a cylinder. Curve (4) shows the linear increase of the furnace temperature. Curves (1), (2) and (3) show the presence of chemical conversions with the absorption and evolution of heat. The temperature drop between the surface and the centre of the cylinder ($R = 25$ mm) during kilning reached 420°C by the end of the process.

Curves (1a), (2a) and (3a) correspond to the same thermocouples at the repeated heating of the same sample up to 1,000°C. As can be seen from the heating curves there are no remaining endothermic phenomena left in the sample. All the three curves show the constant temperature difference in the cylinder since it is heated at a constant rate.

Fig. 3 is the heating curve for the process of kilning the kaolin cylinder. A characteristic picture of the superposition of two thermal effects of different nature can be seen from Fig. 3. At the temperature of 480°C the curve $t_1 = f(\tau)$ deviates to the right and this deviation corresponds to the beginning of the endothermic effect at the cylinder surface. An anological course takes place for the curve $t_2 = f(\tau)$, which a bit later will deviate to the left, and this deviation corresponds to the end of the endothermic effect in the cylinder interior at $x = R/2$. The next few gaps in the temperature curves for these thermocouples (at the furnace temperature equal to 960°C) mark the rise of the exothermal effect at the cylinder surface. At this moment of time the endothermic reaction has not yet reached the central layer of the cylinder as can be seen from the course of the temperature curve $t_3 = f(\tau)$, which shows the rapid growth of the temperature difference between the cylinder surface and its centre. The maximum point on the curve $t_3 = f(\tau)$ marks the end of the endothermal reaction in the centre of the cylinder. The end of the exothermal effect in the kaolin cylinder centre is marked by the second series of gaps of all the temperature curves. Their further position on the thermogram corresponds to the process of heating the body which has no internal heat sources.

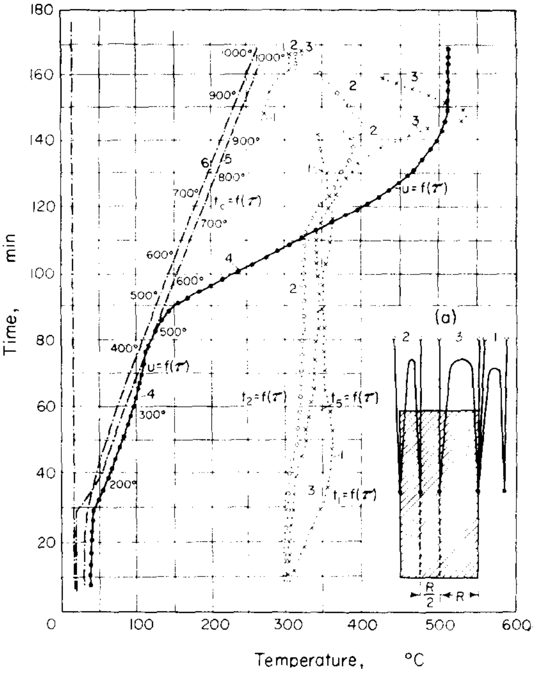

FIG. 3. The curves of heating the cylinder out of kaolin in the kilning process.

The curve of the weight loss $u = f(\tau)$ is given in Fig. 3 (curve 4). The changes in time of the medium temperature of two furnaces are represented by the curves $t_m = f(\tau)$ (see curves 5 and 6). The weight-loss curves of the magnesium hydroxide kilned in the form of cylinders of different sizes are given in Fig. 4.

The linear law of furnace heating allows us to determine the thermal diffusivity coefficient a(m²/hr) and the Biot criterion [1]:

$$a = \frac{bR^2}{\Gamma}\left[\left(\frac{1 - x^2/R^2}{t(R, \tau) - t(x, \tau)}\right)\right] \qquad (1)$$

where b is the heating rate ($b = \mathrm{d}t_m/\mathrm{d}\tau = \text{const}$), Γ is the constant value: for the unlimited plate $\Gamma = 3$ for the cylinder $\Gamma = 4$. The criterion Bi is defined by the formula

$$Bi = \frac{\alpha R}{\lambda} = \frac{2[t(R, \tau) - t(x, \tau)]}{[t_m - t(R, \tau)]\,(1 - x^2/R^2)} \qquad (2)$$

where α is the heat-transfer coefficient

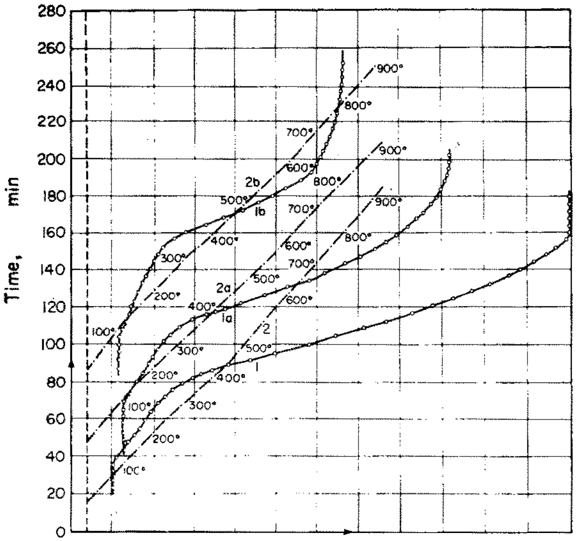

FIG. 4. The curves of weight loss during kilning the cylinders of various sizes, made out of magnesium hydroxide. (1) The weight loss curve (2) The curve of the furnace temperature increase.

(kcal/m² hr °C), λ is the thermal conductivity coefficient (kcal/m hr °C). We can calculate the coefficient a and the criterion Bi from the formulae (1) and (2) for the kilned samples when heating them in a furnace the temperature of which is linearly increasing.

Conditionally we can apply these formulae to the kaolin samples in the process of kilning. In the temperature interval, when the chemical reactions occur, the value of the thermal diffusivity coefficient and the Biot criterion will have the conditional character. Let us define these values through a^* and Bi^*, respectively. The calculation results for the kaolin are given in Table 1. It can be seen from this table that the thermal diffusivity coefficient increases with the temperature rise.

In the temperature interval, where the chemical reactions are negligible, there is almost no difference between the coefficients a and a^*. The Biot criterion is raised with the increase of the temperature t_m, and the Biot criterion in the process of kilning Bi^* is approximately two times smaller than the Biot criterion when the previously kilned samples are heated.

The heater coils, of nichrome wire, were mounted inside of the investigated samples to determine directly the heat-transfer coefficient α, the heat capacity c and the heat of the chemical reaction. Apart from being heated by the furnace the investigated sample could gain additional heat with the help of this coil. The heat of the reaction was determined as follows: a heater coil was mounted inside of the unkilned cylindrical sample along its axis. Two samples were heated simultaneously in the furnace, the unkilned sample with the coil and the kilned one without it. The furnace temperature was increased linearly, the samples were at first heated equally. The mass transfer (the sample weight loss) and the lag in the increase of the temperature, compared with the kilned sample, were observed during the chemical reaction. The rate of heating the unkilned sample was aligned with the kilned one by heating the nichrome wire with an electric current. This process compensated for heat absorbed by the endothermic reaction. It is possible to determine the specific heat of the endothermic reaction through the flow of electric current in the heater coil and through loss of mass by the sample. For the kaolin, for example, the specific heat of the endothermic reaction is equal to 1,230 kcal/kg. The dehydration heat of the magnesium hydroxide is $g = 700$ cal/kg.

Table 1. The thermophysical characteristics of the kaolin

t_m(°C)	100	200	300	400	500	600	700	800	900	1000
$a \times 10^5$ (m²/hr)	108	108	101		101	108	108	116		122
$a^* \times 10^5$		138			125	110			125	
Bi		2·70	2·70	2·70	3·75	4·65	5·00	5·75	5·75	6·84
Bi^*		1·5			1·80			2·50		
α (kcal/m² hr °C)	27	40	50	63	90	120	154	170	190	200
$\lambda \times 10^3$(kcal/m hr °C)	292	391	483	580	642	680	686	702	685	650

This method of the sample heating with the help of the heater coil allows the coefficient α to be determined. For this purpose two kilned samples must be used, one of which has a heater coil attached.†

The two samples are placed in the furnace, the temperature of which increases linearly. Only the temperature of the first sample is recorded. The second sample is heated additionally by the coil so that its surface temperature should always be equal to the ambient temperature (the furnace temperature is $t_2(R, \tau) = t_m$). Then the heat supplied to the sample by the additional heating is obviously equal to the amount of heat Q received by the second sample from the surrounding medium. The total heat-transfer coefficient is

$$\mathrm{d}\alpha = \frac{0{\cdot}86W}{\Delta tA} = \frac{Q}{\Delta tA} \tag{3}$$

where A is the heat-transfer surface of the samples, W is the output of the nichrome coil, Δt is the temperature drop between the samples at their surfaces equal to the temperature drop between the surrounding medium and the surface of the first sample. Having obtained the value of the heat-transfer coefficient α we can determine the specific heat

$$c = 2\alpha[t_m - t(R, \tau)]/b\gamma R \tag{4}$$

where γ is the sample density (kg/m^3).

The thermal conductivity coefficient λ is determined by the formula

$$\lambda = ac\gamma \tag{5}$$

The results of the calculations are given in Table 1. The dependence of the specific heat on temperature is represented in Fig. 5. The dependence of the heat capacity for the unkilned kaolin sample is given in the same Fig. 5 (curve II). The specific heat of the chemical reaction is determined by the total heat capacity and the reaction occurs in the temperature interval from 600° to 800°C.

The analysis of the experimental data shows, that the chemical conversions on heating the body occur at first in the surface layer of the body (the chemical reaction zone). This zone will gradually spread into the interior of the body. The displacement mechanism of the chemical conversion zone in the first approximation may be taken as analogous to the mechanism of deepening the evaporation surface when drying wet solid bodies. This process is sketched in Fig. 6 in the case of the infinite plate $2R$ thick. The concentration of the fixed substance at the plate surface is assumed equal to zero, i.e. $\omega(R, \tau) = 0$.

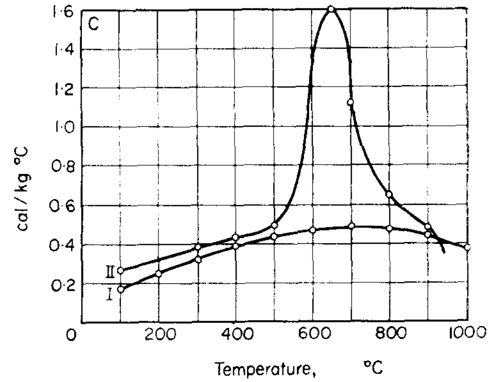

FIG. 5. The dependence of the true (curve I) and the total (curve II) heat capacity of kaolin on temperature.

Let the distance between the lower surface of the chemical conversion layer and the plate surface be ξ, and the diffusion coefficient of the

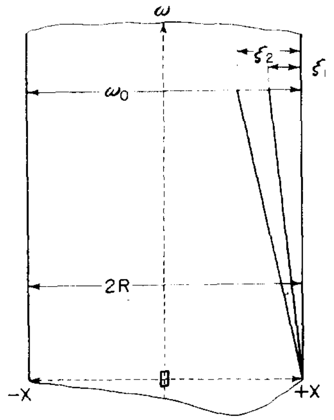

FIG. 6. The scheme for the calculation of the curve of mass-loss kinetics.

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† Usually the coil is joined to the sample before the kilning. The kilning of the sample takes place with the coil attached.

fixed substance through the plate surface layer be k, then we can write

$$-\frac{d\omega}{d\tau}R = \frac{k}{\xi}\omega_0 = \frac{\omega_0}{2}\frac{d\xi}{d\tau} \tag{6}$$

As an approximation we can assume that the decrease in the concentration $\omega(x, \tau)$ in the chemical conversion zone takes place according to the straight-line law (see Fig. 6). From relation (6) we get:

$$\xi = 2\sqrt{(k\tau)} \tag{7}$$

i.e. the conversion surface deepens according to the parabolic law. Moreover, from the relations (6) and (7) we get

$$\frac{\omega}{\omega_0} = 1 - \sqrt{\left(\frac{k\tau}{R^2}\right)} \tag{8}$$

When solving the diffusion problem of fixed substance in a capillary porous body we get an analogous formula with another numerical factor

$$\frac{\omega}{\omega_0} = 1 - \frac{2}{\sqrt{(\pi)}}\sqrt{\left(\frac{k\tau}{R^2}\right)} \tag{9}$$

Using formulae (7) and (8) we can calculate the diffusion coefficient. The following data were marked from the heating kinetics curves for a magnesium hydroxide plate 50 mm thick. ($R = 25$ mm). The dehydration process begins at the average plate temperature equal to 350°C. The time of the displacement of the chemical conversion zone from the surface of the plate to its centre was 40 min. The temperature of the reaction zone was 375°C at the furnace temperature equal to 585°C. Consequently at $\xi = 2{\cdot}5 \times 10^{-2}$ m, $\tau = 0{\cdot}666$ hr. Hence

$$k = \frac{6{\cdot}25}{0{\cdot}666 \times 4} \times 10^{-4} = 2{\cdot}3 \times 10^{-4}\ \text{m}^2/\text{hr}$$

The total mass content was 29·84 g and the weight lost by the plate during 40 min was 16·5 g. Hence we get

$$k = \frac{6{\cdot}25 \times 60(16{\cdot}5)^2}{40 \times (29{\cdot}84)^2} \times 10^{-4} = 2{\cdot}82 \times 10^{-4}\ \text{m}^2/\text{hr}$$

Using the same formula (9) we get

$$k = 2{\cdot}82 \times \frac{\pi}{4} \times 10^{-4} = 2{\cdot}2 \times 10^{-4}\ \text{m}^2/\text{hr}$$

i.e. the two values are quite close.

These calculations prove the established mechanism of the gradual deepening of the zone of chemical reactions in the capillary porous body. The chemical reaction zone is gradually displaced into the interior of the body approximately according to the parabolic law, that coincides with the Stefan law for the freezing of humid bodies.

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