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Původní práce

DETERMINING THE DIFFUSION COEFFICIENT OF WATER VAPOUR IN KAOLIN BODY DURING ISOTHERMAL FIRING IN THE DEHYDROXYLATION REGION; I

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A method was suggested and conditions established for determining the diffusion coefficient of water vapour in a ceramic body during its firing over the dehydroxylation region. The temperature dependence of the diffusion coefficient was determined experimentally; it was found that the diffusion coefficient can be regarded as being independent of concentration.

INTRODUCTION

The approach to the study of firing a ceramic body, containing kaolinite, in the dehydroxylation region, is based on the assumption that dehydroxylation is a 1st-order reaction and that firing is a combined process of mass and heat transfer [1]. Mass transfer is regarded as diffusion with a chemical reaction, and heat transfer as conduction of heat with a source. This approach allowed a mathematical model of this process to be devised; the model can be used to calculate the time development of concentration and temperature fields in the body being fired in the dehydroxylation region.

The resolving of a general model for an actual ceramic mix and body shape requires, among others, knowledge of the material quantities and their dependence on temperature and concentration.

The present study had the aim to work out a method for the determination of the diffusion coefficient which is one of the material quantities needed for the solving of the mathematical model.

The solution of the problem is based on the assumption that dehydroxylation is a first-order chemical reaction producing molecular water from OH^- groups, this being followed by water vapour transfer through the reaction product. Existing findings on the course of dehydroxylation [2 through 4] also indicate that if the process is studied on greater thicknesses of powdered sample layers or those of a body, diffusion of vapours through the decomposition product is regarded as the decisive process of dehydroxylation. The finding given in [5, 6] also shows that an external vapour pressure of 0.006 MPa will slow down the reaction in a significant way.

THEORETICAL

On basing the method for the determination of the diffusion coefficient on the assumptions introduced in the formulation of the mathematical model for body firing over the dehydroxylation range [1] one obtains the following form of mass balance for a binary incompressible mix involving a chemical reaction and free of convective flow:

$$\frac{\partial x_A}{\partial \tau} = \operatorname{div}(D_{AB}(T, x_A) \operatorname{grad} x_A) - k(T)\, x_A, \tag{1}$$

where x_A is the mass ratio of component A, i.e. water bound in the form of OH^- groups in the kaolinite lattice, τ is time, D_{AB} is the diffusion coefficient, T is temperature and k is the rate constant of a first-order chemical reaction, while the temperature dependence of the diffusion coefficient has the form

$$D_{AB} = D_{AB_0} \exp(-B_2/T), \tag{2}$$

where B_2 is the characteristic temperature and D_{AB_0} is a constant.

It is convenient to simplify the resolving of a problem in working out an experimental method. A considerable simplification is brought about by introduction of isothermal conditions while assuming the diffusion coefficient to be independent of concentration, i.e. $D_{AB} \neq D_{AB}(x_A)$. On introduction of these assumptions, balance (1) acquires the form

$$\frac{\partial x_A}{\partial \tau} = D_{AB} \operatorname{div} \operatorname{grad} x_A - k x_A. \tag{3}$$

On assuming a body in the form of an infinite cylinder, then introduction of cylinder ordinates yields the equation

$$\frac{\partial x_A}{\partial \tau} = D_{AB} \frac{\partial^2 x_A}{\partial r^2} + \frac{1}{r} \frac{\partial x_A}{\partial r} - k x_A. \tag{4}$$

The initial and boundary conditions for the solving of non-steady-state isothermal diffusion through an infinite cylinder can then be formulated as follows:

— initial condition

$$x_A(r, 0) = x_{A_0}, \tag{5}$$

— boundary conditions

$$x_A(R, \tau) = x_{A_0} \exp(-k\tau), \tag{6}$$

$$\frac{\partial x_A(0, \tau)}{\partial r} = 0. \tag{7}$$

On solving the balance equation (4) for conditions (5), (6) and (7) numerically by the network method, the time development of concentration profiles in the body has to be calculated while selecting the values of the diffusion coefficient. Subsequent comparison of the calculated time developments of concentration profiles with the experimentally established ones allows the diffusion coefficient value being seeked to be evaluated at a given temperature while at the same time assessing the suitability of the simplifying assumption introduced, i.e. $D_{AB} \neq D_{AB}(x_A)$.

The experimental arrangement of the method should then allow the time development of the concentration profile to be determined for a cylindrical body while conforming to the following conditions:

— attainment of the required temperature and a homogeneous temperature field in the body without any chemical reaction taking place, i.e. during heating up the body the reaction rate is zero,

— it is possible to determine the time corresponding to the reaction onset,
— it is possible to stop the reaction instantaneously in a moment of time required.

Execution of isothermal experiments at various temperatures yields values of diffusion coefficients corresponding to these temperatures and creates conditions for evaluating the temperature dependence of the diffusion coefficient according to equation (2).

EXPERIMENTAL

Cylindrical bodies 32 mm in diameter and 190 mm in length, of Podbořany kaolin and prepared by drawing on a vacuum auger, were used in the experiments. After drying the bodies at 378 K they were baked at 573 K to eliminate possible residues of technologically necessary water and the interlattice molecular water from the illitic-montmorillonitic component of the Podbořany kaolin [8].

The bodies were fired isothermally in the apparatus described in [9] and comprising an analytical balance placed above a vertically shiftable tubular furnace with kanthal winding, a silica glass reactor, a steam generator and a pressure cylinder with compressed air, shown in Fig. 1.

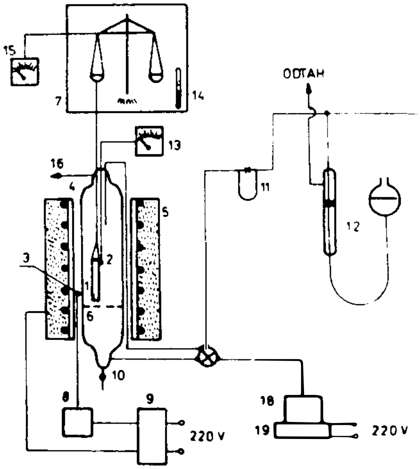

Fig. 1. Schematic diagram of the apparatus for isothermal measurements;
1 — body, 2 — measuring thermocouple at the upper body edge, 3 — control thermocouple, 4 — silica glass reactor, 5 — tubular fnrnace, 6 — wire coils, 7 — analytical balance, 8 — furnace input controls, 9 — autotransformer, 10 — drain cock, 11 — flowmeter, 12 — manostat, 13 — furnace temperature indication, 14 — laboratory thermometer, 15 — indication of temperature at body bottom, 16 — steam outlet, 17 — pressure cylinder, 18 — steam producer, 19 — electric plate.

During heating the bodies up to the required temperature, steam was introduced into the reactor to create a saturated water vapour pressure in the medium and thus to prevent dehydroxylation from taking place during this period. The chemical reaction was regarded as stopped on the basis of constant body weight during the heating up. As soon as a constant temperature and uniform heating-through of the body were attained, the water vapour atmosphere was replaced with air and the decomposition process could take place.

After the holding period, the dehydroxylation was stopped instantaneously by quenching the body down to 298 K (placing it in a desiccator after rapid removal from the furnace). Samples for concentration profile determination were then prepared from the cooled body. The procedure consisted of the following steps:

— a circular slice 10 mm thick was cut from the central part of the body at about one half of the body height,

— a prism was then cut across the diameter and then cut into slices 3 mm thick (Fig. 2),

— the individual elements were dried at 378 K and then fired at 1173 K to constant weight.

The experimental arrangement of the method and the working procedure employed ensured compliance with the conditions set up for the method.

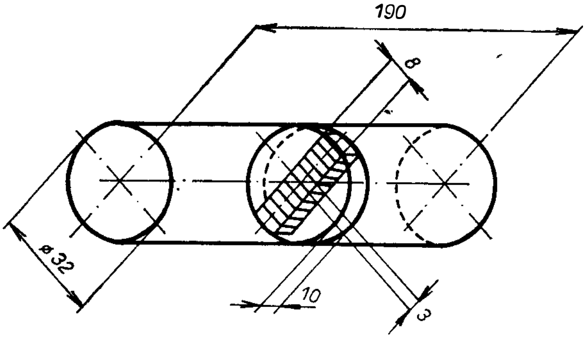

Fig. 2. Schematic diagram of specimen preparation for the determination of concentration fields in the body.

RESULTS

The time development of concentration profiles was determined experimentally at six temperatures over the temperature interval $T \in \langle 733\ \mathrm{K}; 873\ \mathrm{K}\rangle$. Typical profiles obtained are shown for $T = 773$ K and $T = 853$ K in Fig. 3. The diffusion coefficient was calculated in agreement with the procedure of numerical solution of balance equation (4). The boundary condition for the cylinder surface was expressed in the form (6) and the initial condition for all the experiments had the form $x_A(r, 0) = 0.106$ kg/kg. The rate constant of the reaction for a given temperature was calculated from equation (10):

$$k = k_0 \exp\left(-B_1/T\right), \tag{8}$$

using the following values of the constants:

$$B_1 = 21{,}903\ \mathrm{K}; \qquad k_0 = 36\ 034{,}956\ \mathrm{s}^{-1}. \tag{9}$$

Using the chosen diffusion coefficient, the time development of concentration profile best agreeing with the experimental one was calculated. Typical calculated and experimental profiles for $T = 773$ K and $T = 823$ K are plotted in Figs. 4 and 5.

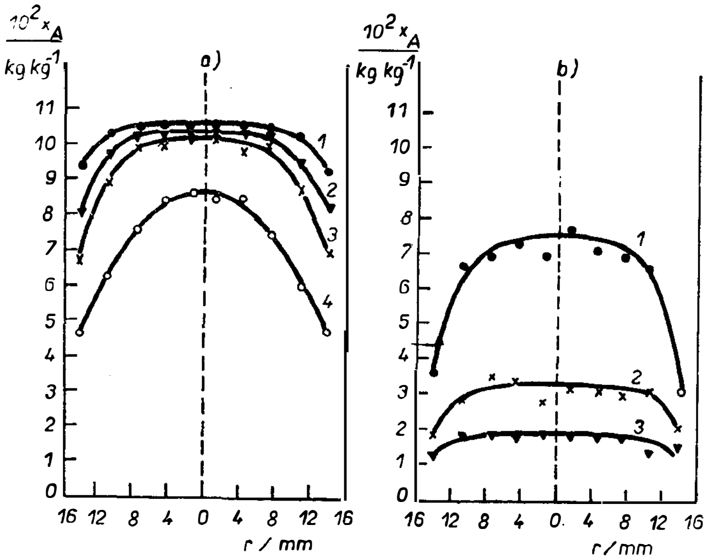

Fig. 3. Experimentally determined time development of concentration profiles in the body during isothermal firing over the dehydroxylation region:
a) firing temperature 773 K, time of holding: 1—3 hrs, 2—6 hrs, 3—9 hrs, 4—20 hrs;
b) firing temperature 853 K, time of holding: 1—3 hrs, 2—4.5 hrs, 3—6 hrs.

The reproducibility of diffusion coefficients determined by the method suggested was also verified at 823 K. At this temperature, the time development of concentration profiles was measured five times for identical time periods. From the values obtained, the mean value was calculated and the mean quadratic error expressed according to the equation

$$\sigma = \sum_{i=1}^{n} (D - D_i)^2 (n - 1)^{-1}, \tag{10}$$

where D is the mean value of the diffusion coefficient and n is the number of value.

It was found that the method allows the value of the diffusion coefficient, which for $T = 823$ K was

$$D_{823} = (6.0 \pm 0.5)\,10^{-9} \qquad [\mathrm{m}^2\,\mathrm{s}^{-1}], \tag{11}$$

to be determined.

DISCUSSION

Quantitative comparison of the calculated and experimental developments of concentration profiles at a given temperature was carried out on the basis of expressing the quadratic error (difference) between the two courses for a given time using the equation

$$\sigma_I = \sum_{i=1}^{n} (x_{Ai}^V - x_{Ai}^{AN})^2/(n - 1), \tag{12}$$

where x_A^V is the calculated concentration and x_A^{AN} is the concentration obtained from the approximation curve of experimental values measured at a given temperature

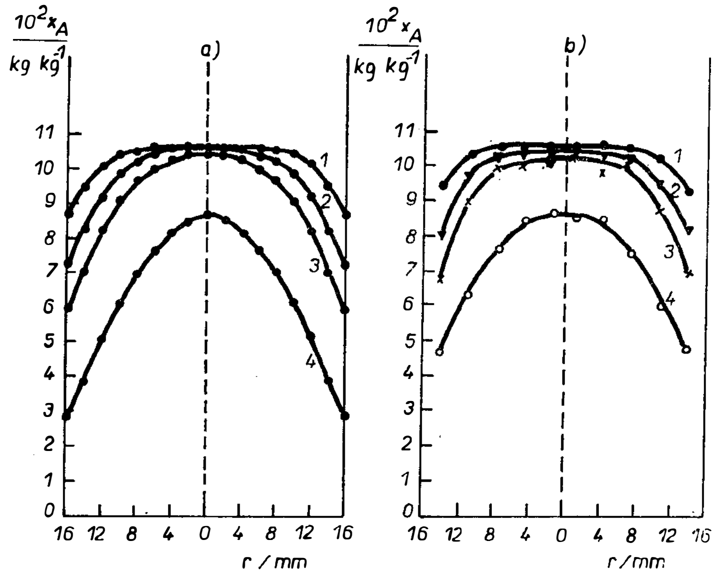

Fig. 4. Comparison of concentration profiles (a) calculated and (b) measured, using the diffusion coefficient value $D = 7.5 \times 10^{-10}$ m^2 s^{-1} at firing temperature of 773 K. The curves with identical numbers correspond to the same time of holding: 1—3 hrs, 2—6 hrs, 3—9 hrs, 4—20 hrs.

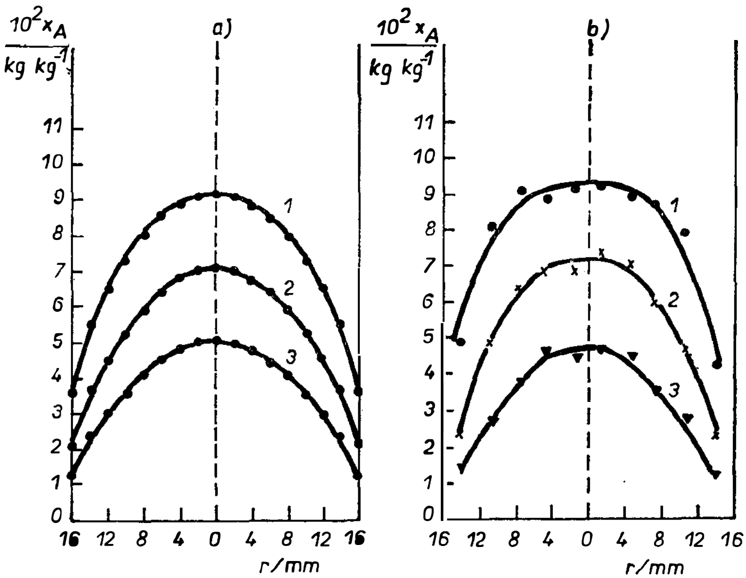

Fig. 5. Comparison of calculated (a) and measured (b) concentration profiles, using the diffusion coefficient value $D = 6.0 \times 10^{-9}$ m^2 s^{-1} at firing temperature of 823 K. The curves with identical numbers correspond to the same time of holding: 1—3 hrs, 2—4.5 hrs, 3—6 hrs.

and time. In addition to this, the square error (difference) between the experimental values of concentration profile x_A^{AN} and the x_A^{AN} values at the same temperatures and time according to the equation

$$\sigma_{II} = \sum_{i=1}^{n} (x_{Ai}^{AN} - x_{Ai}^{N})^2/(n - 1). \tag{13}$$

The calculated σ_I and σ_{II} values at a given temperature of isothermal firing and various times were used to express the significance of introducing the simplifying assumption in the formulation of the method, i.e. the independence of the diffusion coefficient of concentration. A comparison of the two values, e.g. for $T = 773$ K and times over the interval $\tau \in \langle 3 \text{ hrs}; 20 \text{ hrs} \rangle$ is given in Table I.

Comparable relationships between σ_I and σ_{II} were likewise found at 733 K, 798 K, 853 K and 873 K. The comparison of the σ_I and σ_{II} values in Table I implies that the σ_I error exceeds for all the times the σ_{II} deviation respecting the dispersion of experimental data. It may therefore be assumed that deviation σ_I reflects the possible concentration dependence of the diffusion coefficient. However, on assessing the reproducibility of diffusion coefficient determination at $T = 823$ K (cf. equation (11)) and the absolute values of σ_I and σ_{II}, one finds a satisfactory agreement between the time development of calculated and experimentally established concentration profiles, determined with a maximum error of 10 %. The diffusion coefficient can then be regarded as being independent of concentration.

On this assumption, the diffusion coefficients evaluated from the time development of concentration profilesat various temperatures are listed in Table II.

Table I

The values of square errors σ_I and σ_{II} at $T = 773$ K

$\frac{\tau}{h}$	$\frac{\sigma_I \times 10^4}{\text{kg kg}^{-1}}$	$\frac{\sigma_{II} \times 10^4}{\text{kg kg}^{-12}}$
3	0.01	0.01
6	0.14	0.02
9	0.06	0.03
20	0.30	0.01

Table II

The values of diffusion coefficients in terms of temperature

$\frac{T}{K}$	$\frac{D \times 10^{10}}{\text{m}^2\,\text{s}^{-1}}$
733	1.6
773	7.5
798	30
823	60
853	150
873	400

Approximation of these values with the use of equation (2) yielded the values of constants for the temperature dependence of the diffusion coefficient:

$$D_0 = 43{,}045 \text{ m}^2 \text{ s}^{-1}, \qquad B_2 = 24{,}357 \text{ K} \tag{14}$$

which hold over the temperature interval $T \in \langle 733 \text{ K}; 873 \text{ K} \rangle$.

CONCLUSION

The results of the work demonstrated that if the conditions of the experiment are conformed to, the suggested method allows the diffusion coefficient to be determined. The diffusion coefficient characterizing diffusion of water vapour through a kaolin body over the dehydroxylation region, can be considered independent of concentration, and its temperature dependence over the temperature interval $T \in \langle 733 \text{ K}; 873 \text{ K} \rangle$ has the form

$$D = 43{,}045 \exp(-24{,}357 \text{ K/T}) \qquad [\text{m}^2 \text{ s}^{-1}]. \tag{15}$$

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STANOVENÍ DIFÚZNÍHO KOEFICIENTU VODNÍ PÁRY V KAOLINOVÉM TĚLESE PŘI IZOTERMNÍM VÝPALU V OBLASTI DEHYDROXYLACE

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Pro stanovení difúzního koeficientu par vody v tělese při jeho výpalu v oblasti dehydroxylace je vypracována metoda založená na měření časového vývoje koncentračních profilů při izotermním výpalu válce z kaolinu. Jsou určeny podmínky metody pro reprodukovatelné stanovení difúzního koeficientu. Experimentálně je stanovena teplotní závislost difúzního koeficientu ve tvaru (15) platná v teplotním intervalu $T \in \langle 773 \text{ K}; 873 \text{ K} \rangle$. Bylo zjištěno, že difúzní koeficient lze považovat za nezávislý na koncentraci.

Obr. 1. Schéma aparatury pro izotermní měření;
1 — těleso, 2 — měřicí termočlánek u horní podstavy tělesa, 3 — regulační termočlánek, 4 — křemenný reaktor, 5 — trubková pec, 6 — drátěné svitky, 7 — analytické váhy, 8 — regu-

lace příkonu pece, 9 — autotransformátor, 10 — výpustný kohout, 11 — průtokoměr, 12 — manostat, 13 — indikace teploty v peci, 14 — laboratorní teploměr, 15 — indikace teploty u dolní podstavy tělesa, 16 — odvod páry, 17 — tlaková láhev, 18 — vyvíječ páry, 19 — elektrická plotýnka.

Obr. 2. Schéma přípravy vzorků pro určení koncentračního pole v tělese.

Obr. 3. Experimentálně určený časový vývoj koncentračních profilů v tělese při izotermním výpalu v oblasti dehydroxylace;
a) teplota výpalu 773 K, doba výdrže: 1—3 h, 2—6 h, 3—9 h, 4—20 h,
b) teplota výpalu 853 K, doba výdrže: 1—3 h, 2—4,5 h, 3—6 h.

Obr. 4. Porovnání koncentračních profilů vypočtených (a) a naměřených (b) s hodnotou difúzního koeficientu
$D = 7{,}5 \cdot 10^{-10}\ m^2\ s^{-1}$ při teplotě výpalu 773 K. Křivky se stejnými čísly odpovídají témuž času výdrže: 1—3 h, 2—6 h, 3—9 h, 4—20 h.

Obr. 5. Porovnání koncentračních profilů vypočtených (a) a naměřených (b) s hodnotou difúzního koeficientu;
$D = 6{,}0 \cdot 10^{-9}\ m^2\ s^{-1}$ při teplotě výpalu 823 K. Křivky se stejnými čísly odpovídají témuž času výdrže: 1—3 h, 2—4,5 h, 3—6 h.

ОПРЕДЕЛЕНИЕ КОЭФФИЦИЕНТА ДИФФУЗИИ ВОДЯНОГО ПАРА В КАОЛИНОВОЙ МАССЕ ПРИ ИЗОТЕРМИЧЕСКОМ ОБЖИГЕ В ОБЛАСТИ ДЕГИДРОКСИЛИРОВАНИЯ

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Для определения коэффициента диффузии паров воды в массе при ее обжиге в области дегидроксилирования был разработан метод, основывающийся на измерении временного развития концентрационных профилей при изотермическом обжиге цилиндра из каолина. Были установлены условия применения метода для воспроизводимого определения коэффициента диффузии. Экспериментальным путем была установлена температурная зависимость коэффициента диффузии в виде (15), имеющая силу в температурном интервале $T \in \langle 773\ \mathrm{K};\ 873\ \mathrm{K}\rangle$. Было установлено, что коэффициент диффузии можно считать независимым от концентрации.

Рис. 1. Схема аппаратуры для изотермического измерения; 1 — тело, 2 — измерительный термоэлемент у верхней подставки. 3 — регулирующий термоэлемент, 4 — кварцевый реактор, 5 — трубчатая печь, 6 — проволочные бухты, 7 — аналитические весы, 8 — регуляция потребляемой мощности печи, 9 — автотрансформатор, 10 — выпускной кран, 11 — расходомер, 12 — маностат, 13 — индикация температуры в печи, 14 — лабораторный термометр, 15 — индикация температуры у нижней подставки тела, 16 — отвод пара, 17 — баллон, 18 — парообразователь, 19 — электрическая конфорка.

Рис. 2. Схема приготовления образцов, предназначенных для определения концентрационного поля в теле.

Рис. 3. Установленное экспериментальным путем временное развитие концентрационных профилей в теле при изотермическом обжиге в области дегидроксилирования: а) температура обжига 773 К, время выдержки 1—3 часа, 2—6 часов, 3—9 часов, 4 — 24 часа. б) температура обжига 853 К, время выдержки: 1—3 часа, 2—4 часа, 5 часов, 3—6 часов.

Рис. 4. Сопоставление концентрационных профилей, рассчитонных (а) и измеренных (б) с величиной коэффициента диффузии $\mathrm{D} = 7{,}5 \cdot 10^{-10}\ м^2с^{-1}$ при температуре обжига 773 К. Кривые с одинаковыми числами отвечают одинаковому времени выдержки: 1—3 часа, 2—6 часов, 3—9 часов, 4—20 часов.

Рис. 5. Сопоставление концентрационных профилей, рассчитанных (а) и измеренных (б) с величиной диффзуионного коэффициента $\mathrm{D} = 6{,}0 \cdot 10^{-9}\ м^2с^{-1}$ при температуре обжига 823К. Кривые с одинаковыми числами отвечают одинаковому времени выдержки: 1—3 часа, 2—4 часов, 5 часов, 3—6 часов.