Původní práce

THE APPLICATION OF DIFFUSION COUPLE METHOD
TO SATURATED CERAMIC BODIES

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*Transfer of water in a saturated ceramic mixture was investigated by making
diffusion couples of two saturated ceramic bodies with different initial content
of water. Experimental conditions to get reliable diffusion data were determined.
The dependence of the diffusion coefficient on temperature was established; no
correlation was found between D and the content of water.*

INTRODUCTION

Transfer of water in a saturated ceramic mixture is a basic and often rate—controlling process of several technological operations such as slip casting [1], solidifying [2], filter—pressing, aging [3], or drying [4], [5].

Saturated ceramic body is a mixture of ceramic material and water in which no free gas (air) is present. It remains saturated until its water content drops down to the critical value under which the air enters the body. Transfer of water in a saturated ceramic body may be treated as binary diffusion in a mixture of two incompressible components. To describe it quantitatively we need to know the diffusion coefficient as a function of temperature, water content, and other technological variables such as solid component characteristics, deflocculant content, porosity, etc. This function may be measured adopting experimental methods that simply simulate the technological operations with specified initial and boundary conditions. They are based, for example, on ceramic body growth at suspension/plaster interface, on solidifying ceramic body slab with one surface insulated and the other being in contact with gypsum plaster, or on drying a slab or cylinder at quasistationary regime (constant-rate drying). These methods enable us to establish not only diffusion coefficient but also some other important parameters such as the critical, coagulation, or equilibrium moisture [1]—[4].

The basic way to determine the diffusion coefficient is, however, the diffusion couple method [6], [7]. The subject of the present work is the application of that method to saturated ceramic bodies. Our aim is to investigate the conditions for reliable measuring and to determine the dependence of the diffusion coefficient of a saturated ceramic body on its water content and temperature.

THEORETICAL

Composition of ceramic mixtures is usually expressed as the mass ratio, W, of water to dry body. For the purposes of water transfer analysis, it is, however, more suitable to use the volume fraction of water in the mixture, that is,

$$C = (1 + (\varrho_L/\varrho_S) W^{-1})^{-1}, \tag{1}$$

where ϱ_L and ϱ_S are the densities of water and solid component.

The components of saturated ceramic mixture differ in their partial specific volumes. This results in volume changes due to diffusion and brings about motion of the mixture—the relaxation flow. The mass balance of water has, therefore, to include the convective term and hence is of the form [8]:

$$\partial_\tau C + \mathbf{u}. \text{ grad } C + \text{div } \mathbf{h} = 0, \tag{2}$$

where $\mathbf{u}$ is the volume averaged mixture velocity, $\mathbf{h}$ volume flux of water, and ∂_τ partial derivative with respect to time.

The volume flux of water is, generally, a function of several variables,

$$\mathbf{h} = \mathbf{f}(\text{grad } C, \text{ grad } T, \ldots), \tag{3}$$

that is, volume fraction gradient, temperature gradient, relative gravitational or centrifugal forces, etc. In the special situation when only water fraction gradient operate and the function $\mathbf{f}$ is linear and isotropic, the equation (3) reduces to [8]

$$\mathbf{h} = -D \text{ grad } (C - C_E), \tag{4}$$

which is the generalized Fick's first law. Here C_E is the equilibrium volume fraction of water, generally a function of both time and position, and D diffusion coefficeent which depends on moisture, temperature, and technological varibles X_i, that is,

$$D = D(C, T, X_i). \tag{5}$$

Joining (2) and (4), we get the differential equation governing the water distribution in the body:

$$\partial_\tau C + \text{u grad } C = \text{div } (D \text{ grad } (C - C_E)). \tag{6}$$

This equation is the generalized Fick' second law.

In most cases, $C_E = \text{const.}$, so that grad $C_E = 0$ and C_E drops out of equation (6). If, however, the clay structure changes with time or position or both, as it is the case of ion exchange [2c], C_E is no longer constant.

One of the advantages of the diffusion couple method is that, if there is no change of the corss—sectional area of the sample normal to the diffusion direction, the diffusion is onedimensional [6]. For the onedimensional case we may put $\mathbf{u} = \mathbf{0}$, which essentially simplifies the field equation (6). Then the function $D(C)$ can be expressed explicitly as it is done in the well-kown Boltzmann-Matano solution [6] which rests on the assumption that the mixing volume is zero:

$$D = -(2\tau)^{-1}(\mathrm{d}x/\mathrm{d}C) \int_0^C x \, \mathrm{d}C. \tag{7}$$

Here x is the coordinate in the diffusion direction and τ time. In order to evaluate the integral, the knowledge of the position of the so-colled Matano interface is needed.

This difficulty was avoided by Sauer and Freise [9], who, moreover, generalized equation (7) for non-zero mixing volume. Starting from their results, Wagner [7] derived for D the relation

$$D = V(2\tau\,\partial_x Y)^{-1}\left((1-Y)\int_{-\infty}^{x} YV^{-1}\,\mathrm{d}x + Y\int_{x}^{\infty}(1-Y)\,V^{-1}\,\mathrm{d}x\right), \qquad (8)$$

where V is the partial specific volume of water, ∂_x is the partial derivative with respect to x, and Y is definied as

$$Y = (C-C_1)\,/\,(C_2-C_1) \qquad (9)$$

with C_1 and C_2 being the initial volume fractions of water such that $C_2 > C_1$. For incompressible components, $V = \mathrm{const.}$, and equation (8) simplifies to

$$D = (2\tau\,\partial_x Y)^{-1}\left((1-Y)\int_{x_1}^{x} Y\,\mathrm{d}x + Y\int_{x}^{x_2}(1-Y)\,\mathrm{d}x\right). \qquad (10)$$

In this equation, the infinite integration limits were substituted by the finite values x_1 and x_2 at which Y reaches its limiting values, that is, 0 or 1.

If D is independent of C, we have simple solution

$$Z = \mathrm{erf}\left(\frac{1}{2}\,x(D\tau)^{-1/2}\right), \qquad (11)$$

where

$$Z = (C-C_\mathrm{S})\,/\,(C_{1,2}-C_\mathrm{S}) \qquad (12)$$

with C_S being the volume fraction of water at the Matano surface, which is easy to determine because of the curve Z vs. x symmetry.

EXPERIMENTAL

Using a vacuum auger, electrical porcelain with augmented content of α-Al_2O_3 was formed into cylinders 3 cm in diameter or prisms wit 3×3 cm cross-section ,both 10 cm in length. The bodies were carefully insulated to avoid exchange of water between them and their environment and exposed for about 40 minutes to working temperature. Then, two by two, each with different water content, the bodies were joined by their bases, from which the insulation had been removed, to form couples, the joints were insulated and the couple exposed for about 1 to 24 hours to the temperature to which they had been preheated. After given periods of time, the couples were quickly cooled and cut into cca 1 mm slices to determine their water content distribution.

It was found out that if the measuring should be reliable, the following conditions have to be satisfied:

(i) high degree of homogeneity,
(ii) high quality of insulation,
(iii) individual tempering of parts,
(iv) perfect joint,
(v) quick cooling.

CALCULATIONS AND RESULTS

It was at first assumed that the diffusion coefficient depends on the volume fraction of water by the relation

$$D^{-1} = D_1^{-1}C + D_2^{-1}(1 - C), \qquad (13)$$

where D_1 and D_2 are constants, according to which the diffusion resistance of mixture is the sum of diffusion resistances of its components. However, the experimental curves C vs. x (Fig. 1) were best fitted with $D_1 = D_2 = D = $ const., which means that, within the experimental accuracy, D was independent of water content.
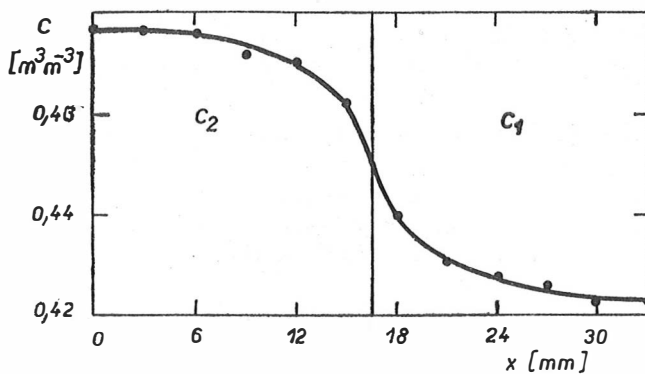

Fig. 1. Water content distribution in a diffusion couple.

To support this conclusion, a set of couples with different initial water content was measured at $T = 293$ K. Again, no significant correlation between D and C was observed. The independence of D on C enabled us to calculate D using the relation (11).

Table I

Diffusion data

$W_2 \cdot 10^2$	$\Delta W_{2-1} \cdot 10^2$	$\dfrac{T}{K}$	$\dfrac{\bar{D} \cdot 10^9}{m^2\,s^{-1}}$	$\dfrac{\sigma \cdot 10^{10}}{m^2\,s^{-1}}$
31 30 26	8 5 3	293	0,14 0,15 0,14	0,4
30	5	309	6,2	4,3
26	3	318	8,2	4,8
26	3	328	11,8	5,2

Experimantal results are shown in Tab. I. The initial water content of one of the couple parts and the initial water content difference expresed in % of dry mass are shown in the first two columns. The third column shows the mean diffusion coefficient and in the last column the values of

$$\delta = (\sum_{i=1}^{n} (D_i - D_{mean})^2 (n-1)^{-1})^{-1/2}$$

are given.

An Arrhenius equation forced to the data yields

$$D = D_0 \exp(-B/T) \tag{14}$$

with $D_0 = 1.78 \times 10^9$ m² s⁻¹ and $B = 1.27 \times 10^4$ K. It should be noted, however, that the fit of Arrhenius behaviour is poor.

CONCLUSIONS

1. The diffusion couple method is suitable for reliable measurement of diffusion coefficients in saturated ceramic bodies.

2. In an electrical porcelain saturated body no correlation between diffusion coefficient and water content was found; it seems likely that this conclusion may be generalized to all saturated ceramic bodies.

3. In the temperature interval 293 to 328 K, $D = D_0 \exp(-B/T)$ with $D_0 = 1.78 \times 10^9$ m² s⁻¹ and $B = 1.27 \times 10^4$ K for the body used, but the fit of Arrhenius behaviour was poor.

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MĚŘENÍ DIFÚZNÍHO KOEFICIENTU V NASYCENÉ KERAMICKÉ SMĚSI METODOU DIFÚZNÍHO PÁRU

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V práci je na studium difúze vody v nasycené keramické směsi aplikována metoda difúzního páru a ukázán postup vyhodnocení difúzního koeficientu. Pro spolehlivost stanovení difúzního koeficientu popsanou metodou byly experimentálně určeny tyto podmínky: a) dokonalost spojení těles v difúzním páru, b) vyhovující kvalita izolační vrstvy, c) samostatné prohřátí těles na požadovanou teplotu a konstantnost teploty po celou dobu difúze, d) rychlé schlazení difúzního páru po ukončení difúze před jeho rozřezáním a e) reprodukovatelná příprava těles s počátečním homogenním rozložením vlhkosti. Ze stanovených hodnot difúzních koeficientů vyplynulo, že ve vodou nasyceném keramickém tělese je D nezávislý na vlhkosti a jeho teplotní závislost pro sledovanou směs technického porcelánu v intervalu teplot 293—328 K je popsána vztahem:

$$D = D_0 \exp(-B/T),$$

$$D_0 = 1,78 . 10^9 \text{ m}^2 \text{ s}^{-1}, \quad B = 1,27 . 10^4 \text{ K}.$$

Obr. 1. Rozdělení vlhkosti v difúzním páru.

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ИЗМЕРЕНИЕ КОЭФФИЦИЕНТА ДИФФУЗИИ В НАСЫЩЕННОЙ КЕРАМИЧЕСКОЙ СМЕСИ МЕТОДОМ ДИФФУЗИОННОЙ ПАРЫ

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Для исследования диффузии воды в насыщенной керамической смеси применяется метод диффузионной пары и приводится способ оценки диффузионного коэффициента. Для надежности определения диффузионного коэффициента с помощью сверх приводимого метода экспериментально устанавливаются следующие условия: а) совершенность соединения тел в диффузионной паре, б) пригодное качество изоляционного слоя, в) самостоятельный прогрев тел до требующей температуры и постоянность температуры по все время диффузии, г) быстрое охлаждение диффузионной пары после окончания диффузии перед его разрезкой и д) воспроизводимое приготовление тел с исходным однородным распределением влажности. Из установленных величин диффузионных коэффициентов следует, что в насыщенном водой керамическом теле D не зависит от влажности и его температурная зависимость для исследуемой смеси технического фарфора в интервале температур 293—328 К описывается отношением:

$$D = D_0 \text{ экс } (-B/T),$$

$$D_0 = 1{,}78 \cdot 10^9 \text{ м}^2\text{с}^{-1}, \; B = 1{,}27 \cdot 10^4 \text{ К}.$$

Рис. 1. Распределение влажности в диффузионной паре.