Silikáty 27, s. 107—113 (1983)

TEMPERATURE DEPENDENCE OF THE THERMODIFFUSION COEFFICIENT OF WATER IN A CERAMIC MIX

JIŘÍ HAVRDA, FRANTIŠEK OUJIŘÍ, BOŽENA KOFROŇOVÁ

Department of the Technology of Silicates, Institute of Chemical Technology, Suchbátarova 5, 166 28 Prague 6

Received 9. 7. 1982

The method of two thermal sources was applied to the study of water transfer due to temperature gradient in a saturated ceramic mix at various temperatures. The temperature dependence of the thermodiffusion coefficient was expressed and its value, with the calculation procedure employed, was found to be independent on the temperature gradient.

INTRODUCTION

A quantitative description of the effect of temperature gradient on water transfer in a saturated ceramic mix requires knowledge of the thermodiffusion coefficient and of its temperature dependence. Combined with knowledge of the concentration and temperature dependence of the diffusion coefficient and of thermal conductivity, this provides input data for transfer equations describing the transfer of water in a saturated ceramic mix under the joined effects of concentration and temperature gradients. Solution of these equations permits to give an idea of the significance of temperature gradient for the given process. In a number of instances it is thus possible to reduce the number of boundary conditions in the problem and thus to simplify the mathematical solution of complex technological operations involved in the manufacture of ceramics including water transfer. The method of two thermal sources was developed for the determination of the thermodiffusion coefficient of water, and conditions were established for its reliable determination [1]. Using this method, the thermodiffusion coefficient of water was determined in a saturated porcelain mix at one mean temperature, $\bar{T} = 319.6$ K.

The present work had the aim to determine the temperature dependence of the thermodiffusion coefficient in a water-saturated ceramic mix with a saturated boundary, i. e. in a closed system. The following two experimental arrangements were used for determining the effect of temperature on the thermodiffusion coefficient value:

(i) the mean body temperature $\bar{T}$ was measured at a constant temperature gradient;

(ii) the temperature gradient was measured at a constant $\bar{T}$ of the body.

THEORY

When regarding a water-saturated ceramic mix as a binary mixture of two incompressible components, then under isobaric conditions and in the absence of external forces, and if the structure of the solid component is homogeneous and constant, in a steady state ($\mathbf{h} = \mathbf{0}$, $\partial C/\partial \tau = 0$, $\partial T/\partial \tau = 0$, where $\mathbf{h}$ is the volume moisture flow, C is the volume moisture content, T is temperature and τ is time) the equation for volume flow of moisture for a one-dimensional problem has the form:

$$D\,\mathrm{d}C/\mathrm{d}x = -D_T\,\mathrm{d}T/T\,\mathrm{d}x, \tag{1}$$

where D is the diffusion coefficient, D_T is the termodiffusion coefficient and x is the coordinate in the direction of diffusion. For the temperature profile in a plate-shaped body L in thickness for a one-dimensional problem and constant conductivity, solution of the Fourier—Kirchhoff equation for boundary conditions [3]:

$$\begin{matrix} x = 0,\ T = T_1, & \\ & T_1 > T_2 \\ x = L,\ T = T_2, & \end{matrix} \tag{2}$$

yields the following equation:

$$T = T_1 - ((T_1 - T_2)\,x/L. \tag{3}$$

When neglecting the temperature dependence D and D_T, then with conditions (2) hold the following boundary conditions:

$$\begin{aligned} x = 0,\ C = C_1, \\ x = L,\ C = C_2, \end{aligned} \tag{4}$$

and on relating the values D and D_T to the mean temperature given by the equation

$$\bar{T} = (T_1 + T_2)\,/2, \tag{5}$$

then the relationship $C = f(x)$ has the form

$$C = C_1 + ((C_2 - C_1)\,x/L) \tag{6}$$

and the following equation holds for the calculation of D_T:

$$D(C_2 - C_1)/L = D_T(T_1 - T_2)/\bar{T}L. \tag{7}$$

THE METHOD OF TWO THERMAL SOURCES AND THE MEASURING PROCEDURE

The method, involving one-dimensional thermodiffusion, is based on establishing and determining a constant temperature profile in the body, as described by equation (3). The resulting moisture profile described by conditions (4) is determined in the steady state. On approximating its course according to equation (6), C_1 and C_2 are evaluated and D_T is calculated from equation (7) under the given simplifying assumptions. The diffusion coefficient D value was calculated from its temperature dependence in the form $D = 5.52 \times 10^{11} \exp(-14\,484\ \mathrm{K}/T)\ \mathrm{m^2\,s^{-1}}$. This relationship was established by the diffusion couple method for the same ceramic mix [4]. The temperature dependence of D_T was determined on prism-shaped elements having the sizes $L = 1.2 \times 10^{-2}$ m, $a = 4 \times 10^{-2}$ m and $b = 10 \times \times 10^{-2}$ m. The bodies were prepared by extrusion of a saturated porcelain mix with an addition of α-Al_2O_3 on a vacuum auger press. After forming, the bodies were insulated and placed for 48 hours in a water-saturated medium to equalize the moisture distribution throughout the body volume. The isolated body was then placed between two copper prisms having constant temperatures T_1 and T_2 and left in this pre-set temperature gradient for 7 hours. Then followed cooling down to $T = 276$ K, removal of the insulation and cutting into slices 1.2×10^{-3} m in thickness in the direction of L for moisture profile determination. The temperature profile in the body was measured by four thermocouples (copper-constantan) in differential connection. The same procedure was used at all the working temperatures $\bar{T}$ and at all the temperature gradients.

RESULTS

Both the mositure and temperature profiles in the body were measured four times at each $\bar{T}$ or grad T. The D_T established for the $\bar{T}$ and grad T, were averaged and their standard deviation was expressed:

$$\sigma = \left(\sum_{i=1}^{n} (\bar{D} - D_{\mathrm{i}})^2 (n - 1)^{-1} \right)^{1/2}. \tag{8}$$

The typical moisture and temperature profiles measured with arrangement (i), i. e. at various $\bar{T}$ and at grad T = const., are plotted in Fig. 1. The mean values of $\bar{D}_T$ for the working $\bar{T}$ are listed in Table I. The measurements at $\bar{T}$ = const. and at varying grad T (arrangement (ii)) were carried out for two mean temperatures $\bar{T} = 310.5$ K, $\bar{T} = 327.7$ K. The moisture and temperature profiles are plotted in Figs. 2 and 3. The calculated $\bar{D}_T$ for the working grad T are listed in Table II for both $\bar{T}$. For the given $L = 1.2 \cdot 10^{-2}$ m, the temperature difference

Table I

Mean $\bar{D}_T$ values for various $\bar{T}$ at $\Delta T = 25.1$ K

$\frac{T}{K}$	$\frac{\bar{D}_T \cdot 10^{10}}{\mathrm{m^2\,s^{-1}}}$	$\frac{\sigma \cdot 10^{10}}{\mathrm{m^2\,s^{-1}}}$
299.4	0.4	0.1
310.5	3.0	1.0
319.6	6.0	1.0
327.1	28.0	12.0
333.5	59.0	12.0

Table II

The mean $\dot{D}_T$ for various ΔT at two $\bar{T}$ = const.

$\frac{T}{K}$	$\frac{\Delta T}{K}$	$\frac{\dot{D}_T \cdot 10^{10}}{\mathrm{m^2\,s^{-1}}}$	$\frac{\sigma \cdot 10^{10}}{\mathrm{m^2\,s^{-1}}}$
310.5	18.6	2.0	1.0
	21.1	2.0	0,9
	26.7	3.0	1.0
327.7	21.7	29.0	10.0
	26.2	28.0	12.0
	32.7	34.0	5.0

$\Delta T = T_1 - T_2$ is specified in the Table and in the Figures in place of grad T. Because the moisture and temperature profiles exhibited the same agreement in all the measurements within the framework of errors, profiles from one experiment only are given for each T and grad T.

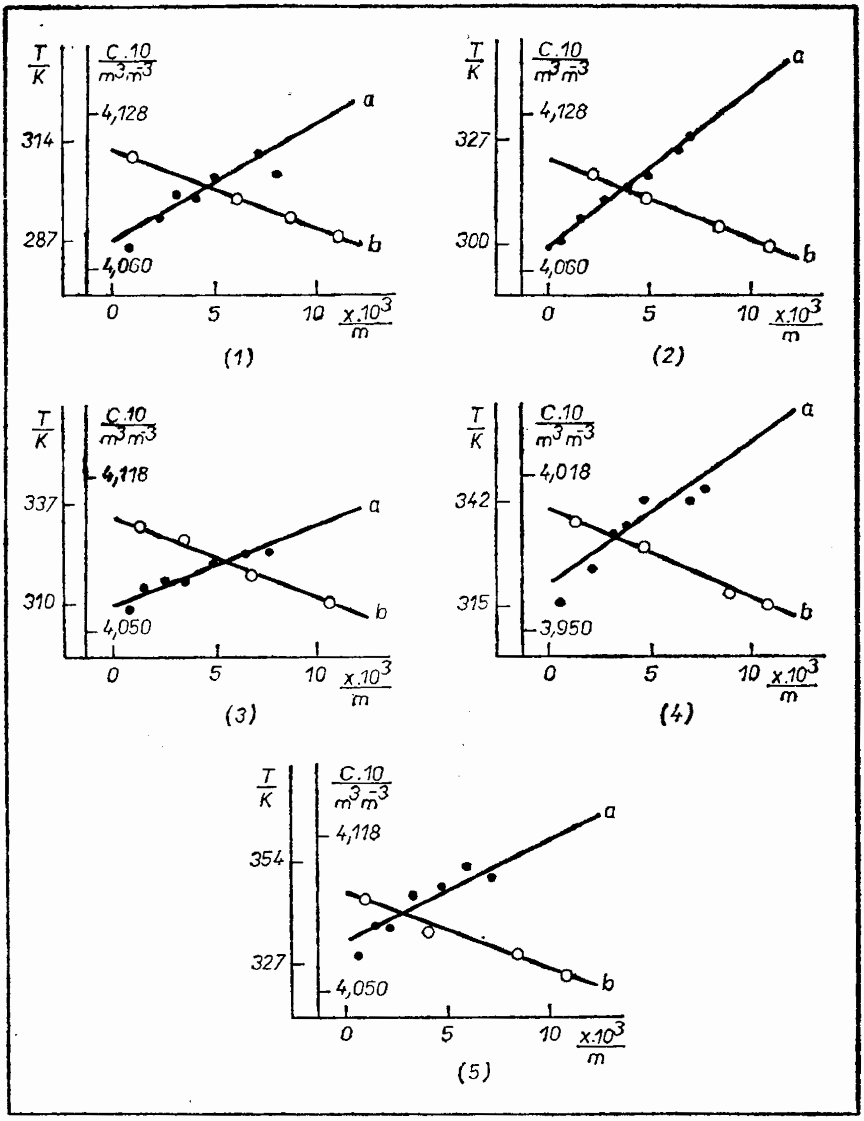

Fig. 1. Volume moisture content and temperature distribution in a body at $\Delta T = 25.1$ K; 1 — $T = 299.4$ K, 2 — $T = 310.5$ K, 3 — $T = 319.6$ K, 4 — $T = 327.1$ K, 5 — $T = 333.5$ K, a — moisture profile, b — temperature profile.

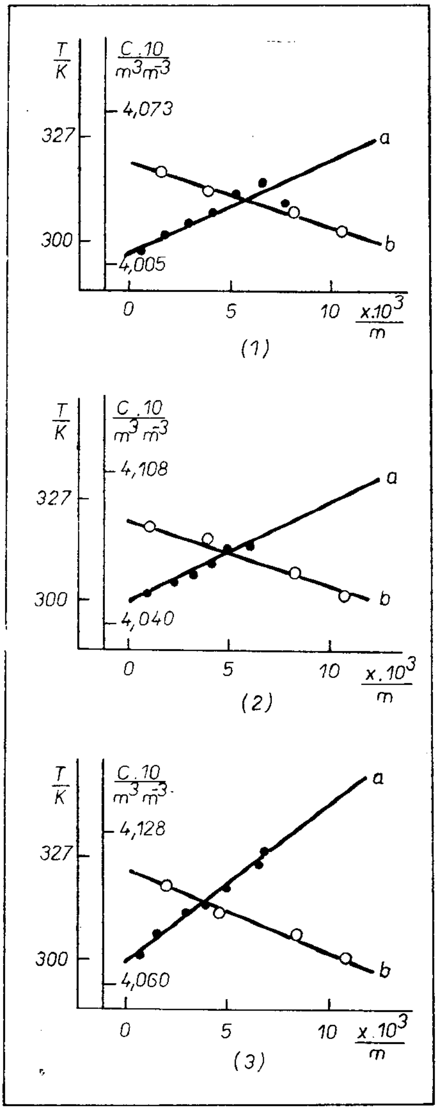

Fig. 2. Distribution of volume moisture and temperature in the body at $T = 310.5$ K; 1 — — $\Delta T = 18.6$ K, 2 — ΔT 21.1 K, ΔT 3 — = = 26.7 K, a — moisture profile, b — temperature profile.

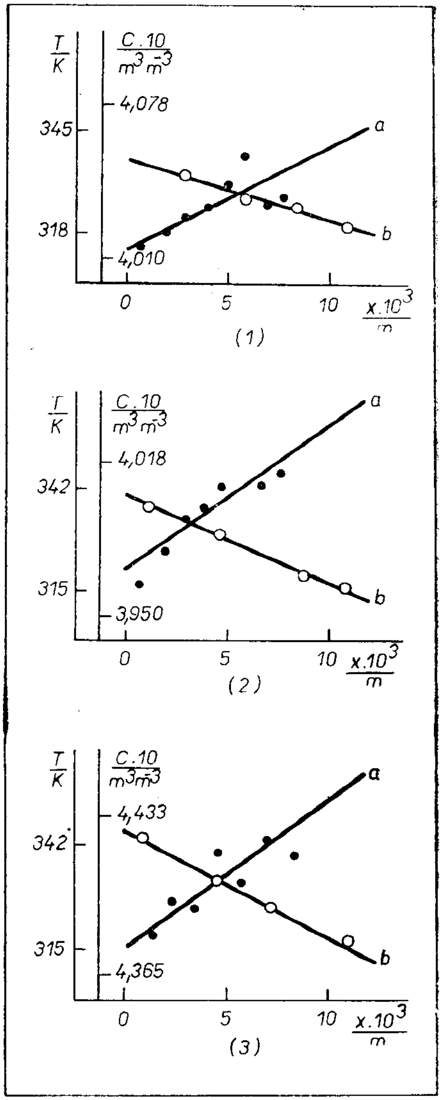

Fig. 3. Volume moisture and temperature distribution in the body at $T = 327.7$ K; 1 — $\Delta T = 21.7$ K, 2 — $\Delta T = 26.2$ K, 3 — $\Delta T = 32.7$ K, a — moistureprofile, b — temperature profile.

DISCUSSION AND CONCLUSION

The temperature dependence of $\bar{D}_T$ in the temperature interval $\bar{T} \in \langle 299.4\text{K}, 333.5\text{ K}\rangle$ was approximated by the following equation for the values listed in Table I:

$$\bar{D}_T = D_{0T} \exp(-B_1/\bar{T}), \tag{9}$$

where B_1 is the characteristic process temperature and D_{0T} is a constant. The values of the constants in equation (9) are the following:

$$D_{0T} = 3.19 \times 10^{10}\ \mathrm{m^2\,s^{-1}},\ B_1 = 14\,397\ \mathrm{K}. \tag{10}$$

A comparison of the $\bar{D}_T$ values in Tables I and II shows that the $\bar{D}_T$ measured at the same $\bar{T}$ but at various grad T are virtually identical. This means that for expressing the temperature dependence of D_T the condition of maintaining a constant T in all the experiments is not necessary (arrangement (i)) in calculating D_T according to equation (7).

On the basis of the experiments performed, the findings on the thermodiffusion of water in a saturated porcelain mix can be summarized into the following points:

1. In the simplified calculation of D_T, the D_T value does not depend on grad T.
2. The temperature dependence of D_T in the temperature range is described by equation (9) where the values of the constants are given by equation (10).

References

[1] Havrda J., Oujiří F., Macháček J.: Silikáty, 26, 299 (1982).

[2] De Groot S. R., Mazur P.: *Non-Equilibrium Thermodynamics.* North-Holland, Amsterdam 1962.

[3] Carslaw H. S., Jaeger J. C.: *Conduction of Heat in Solids.* Clarendon Press, Oxford 1959.

[4] Havrda J., Oujiří F.: Silikáty *26*, 3, 203 (1982).

TEPLOTNÍ ZÁVISLOST TERMODIFÚZNÍHO KOEFICIENTU VODY V KERAMICKÉ SMĚSI

Jiří Havrda, František Oujiří, Božena Kofroňová

Katedra technologie silikátů, Vysoká škola chemicko-technologická, 166 28 Praha

Přenos vody vlivem teplotního gradientu v nasycené keramické směsi za různých teplot byl studován metodou dvou tepelných zdrojů. Byl proměřen jednak (i) vliv teploty na přenos vody při konstatním gradientu teploty a jednak (ii) vliv gradientu teploty při konstatní střední teplotě tělesa. Z proměřených vlhkostních a teplotních profilů byl vypočten termodifúzní koeficient. Bylo zjištěno, že jeho hodnota nezávisí pro použitý způsob výpočtu na hodnotě gradientu teploty. Teplotní závislost termodifúzního koeficientu pro sledovanou nasycenou porcelánovou směs v proměřovaném rozmezí středních teplot $\bar{T} \in \langle 299{,}4\ \mathrm{K}, 333{,}5\ \mathrm{K}\rangle$ byla vyjádřena vztahem

$$\bar{D}_T = D_{0T} \exp\left(-B_1/\bar{T}\right),$$

s hodnotami konstant

$$D_{0T} = 3{,}19 \,.\, 10^{10}\ \mathrm{m^2\,s^{-1}}\ \text{a}\ B_1 = 14\,397\ \mathrm{K}.$$

Obr. 1. Rozložení objemové vlhkosti a teploty v tělese při $\Delta T = 25{,}1$ K, 1 — $\bar{T} = 299{,}4$ K, 2 — $\bar{T} = 310{,}5$ K, 3 — $\bar{T} = 319{,}6$ K, 4 — $\bar{T} = 327{,}1$ K, 5 — $\bar{T} = 333{,}5$ K, a — vlhkostní profil, b — teplotní profil.

Obr. 2. Rozložení objemové vlhkosti a teploty v tělese při $\bar{T} = 310{,}5$ K; 1 — $\Delta T = 18{,}6$ K, 2 — $\Delta T = 21{,}1$ K, 3 — $\Delta T = 26{,}7$ K, a — vlhkostní profil, b — teplotní profil.

Obr. 3. Rozložení objemové vlhkosti a teploty v tělese při $\bar{T} = 327{,}7$ K; 1 — $\Delta T = 21{,}7$ K, 2 — $\Delta T = 26{,}2$ K, 3 — $\Delta T = 32{,}7$ K, a — vlhkostní profil, b — teplotní profil.

ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ТЕРМОДИФФУЗИОННОГО КОЕФФИЦИЕНТА ВОДЫ В КЕРАМИЧЕСКОЙ СМЕСИ

Иржи Гаврда, Франтишек Оуиржи, Божена Кофронева

Кафедра технологии силикатов, Химико-технологический институт, 166 28 Прага

Перенос воды под влиянием температурного градиента в насыщенной керамической смеси при разных температурах исследовали с помощью метода двух термических источников. Измеряли как влияние температуры на перенос воды при постоянном градиенте температуры (i), так и (ii) влияние градиента температуры при постоянной средней температуре тела. Из измеренных профилей влаги и температуры рассчитали коэффициент термодиффузии. Было установлено, что его величина не зависит при данном способе рассчета от величины градиента температуры. Температурная зависимость коэффициента термодиффузии для исследуемой насыщенной фарфоровой смеси в измеряемых пределах средних температур $T \in <299{,}4$ К, $333{,}5$ К $>$ выражается шением:

$$\bar{D}_T = D_{0T}\,\text{эксп}(-B_1/T),$$

с величинами констант:

$$D_{0T} = 3{,}19 \,.\, 10^{10}\,\text{м}^2\text{с}^{-1} \quad \text{и} \quad B_1 = 14\,397\ \text{К}.$$

Рис. 1. Распределение объемной влажности и температуры в теле при $\Delta T = 25{,}1$ К. 1 — $T = 299{,}4$ К, 2 — $T = 310{,}5$ К, 3 — $T = 319{,}6$ К, 4 — $T = 327{,}1$ К 5 — $T = 333{,}5$ К, a — профиль влажности, b — профиль температуры.

Рис. 2. Распределение объемной влажности и температуры в теле при $T = 310{,}5$ К. 1 — $\Delta T = 18{,}6$ К, 2 — $\Delta T = 21{,}1$ К, 3 — $\Delta T = 26{,}7$ К, a — профиль влажности, b — профиль температуры.

Рис. 3. Распределение объемной влажности и температуры в теле при $T = 327{,}7$ К. 1 — $\Delta T = 21{,}7$ К, 2 — $\Delta T = 26{,}2$ К, 3 — $\Delta T = 32{,}7$ К, a — профиль влажности, b — профиль температуры.

RICKET H.: ELECTROCHEMISTRY OF SOLIDS, AN INTRODUCTION

(Elektrochemie pevných látek, úvod). Springer-Verlag, Berlin—Heidelberg—New York 1982. 240 str., vč. 95 obr. a 23 tab. Cena 248 DM, 68,90 US $.

Jako 7. svazek řady Inorganic Chemistry Concepts vychází dílo předního západoněmeckého odborníka v oboru fyzikální chemie, týkající se elektrochemie pevných látek. Jde o přepracovanou a podstatně doplněnou monografii téhož autora „Einführung in die Elektrochemie fester Stoffe“, vydanou v roce 1973.

Kniha v prvých šesti kapitolách obsahuje úvodní pasáže, týkající se fyziky a chemie vzniku poruch v pevných látkách, pohyblivosti a difúze elektronů a iontů. Druhá část sestávající též ze šesti kapitol se soustřeďuje na iontové vodiče a jejich aplikaci. Ukazuje příklady pevných elektrolytů, články s pevnými elektrolyty a jejich použití pro termodynamická a kinetická měření a další možnosti praktické aplikace.

Zajímavé kapitoly tvoří elektrochemické aplikace v oblasti reakcí v pevném stavu, transportní jevy v neizotermních systémech a vznik termoelektrického napětí. Doplněny oproti vydání v německém jazyce jsou především kapitoly podávající přehled o iontových pevných vodičích různých typů a technických aplikacích pevných elektrolytů.

Publikace představuje vynikající učebnici. Je doplněna bohatým matematickým aparátem a řadou praktických příkladů. Lze ji doporučit především vědeckým a odborným pracovníkům v oblasti elektrických vlastností pevných látek, termodynamiky a kinetiky reakcí v pevné fázi.

J. Kutzendörfer