

Původní práce

BARODIFFUSION OF WATER IN CERAMIC MIX

JIŘÍ HAVRDA, FRANTIŠEK OUJŘÍ, MARIE ŽIŽKOVÁ

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

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A method has been worked out and conditions determined for reliable determination of the barodiffusion coefficient of water in a saturated ceramic mix in plastic state. Its value was determined experimentally for a water-saturated porcelain mix at 393 K, and compared with the calculated value.

INTRODUCTION

The approach towards the solution considering the transfer of water in a saturated ceramic mix as a diffusion in a binary mixture of two incompressible components indicates that the gradient of concentration, temperature and pressure is generally the driving force of water transfer. A study on the effect of the state of surface of a water-saturated ceramic body on water transfer under isothermal conditions provided the conclusion that the pressure gradient inside the body is caused by capillary barodiffusion, i.e. by capillary suction of water in the menisci on the non-saturated surface. The volume flow of moisture in the body in the case of a one-dimensional problem is then given by the equation:

$$h = -D_{\text{ef}}(\partial C/\partial x), \quad (1)$$

where C is the volume moisture content, x is the ordinate in the direction of diffusion, and D_{ef} is the effective diffusion coefficient including the influence of concentration diffusion as well as of capillary barodiffusion. This means that the following equation holds for the volume flow of moisture:

$$h = -D(\partial C/\partial x) - D_p(\partial P/\partial x), \quad (2)$$

where D is the coefficient of diffusion, D_p is the coefficient of barodiffusion and P is pressure.

When the mean size of capillaries in the body is known, the difference in pressure can be expressed from Laplace's equation:

$$\Delta P \approx 2\gamma r^{-1} \quad (3)$$

where γ is the surface tension of water and r is the mean capillary radius. By joining equations (1), (2) and (3) the following expression is obtained for the calculation of the barodiffusion coefficient for an equalized process and a body of small size:

$$D_p = (2\gamma)^{-1} (D_{\text{ef}} - D) \Delta C r. \quad (4)$$

Using experimentally determined values of D_{ef} , D , ΔC , r and γ at $T = 293$ K,

the barodiffusion coefficient value for the given water-saturated porcelain mix was expressed as follows [1]:

$$D_p = 1.5 \times 10^{-14} \text{ m}^2\text{s}^{-1}\text{Pa}^{-1}. \quad (5)$$

The present study had the aim to verify experimentally the reliability of D_p calculation using the procedure outlined above, i.e. to work out a method for a reliable determination of the barodiffusion coefficient.

**DETERMINING THE BARODIFFUSION COEFFICIENT
BY SUCTION OF WATER THROUGH A LAYER OF GRANULAR
MATERIAL**

A pressure and moisture gradient is developed inside the body L in length under isothermal conditions when water is sucked through unidimensionally. The process acquires a steady state after a certain period of time, i.e. $h = \text{const.}$ and the volume flow of moisture through the body is described by the equation [2]:

$$h = -D(dC/dx) - (D'_p/P) (dP/dx). \quad (6)$$

When D and D'_p are constant, solution of (6) for the conditions:

$$\begin{aligned} x = 0, C = C_1, P = P_1, \\ x = L, C = C_2, P = P_2 \end{aligned} \quad (7)$$

yields:

$$D'_p = (D(C_1 - C_2) - hL)/\ln(P_2/P_1), \quad (8)$$

and the pressure and moisture profile in the body has the form:

$$P = P_1 \exp((-x \ln(P_1/P_2))/L), \quad (9)$$

$$C = C_1 - ((C_1 - C_2) x)/L. \quad (10)$$

When the mean integral pressure is defined as:

$$\bar{P} = L^{-1} \int_0^L P dx, \quad (11)$$

then by joining (9) and (11) and by subsequent integration, the following equation is obtained for the mean pressure:

$$\bar{P} = (P_1 - P_2)/\ln(P_1/P_2). \quad (12)$$

The barodiffusion coefficient value can then be related to the medium pressure. Equations (9) and (10) therefore indicate that at steady state, a linear moisture distribution and an exponential pressure distribution occurs in a body in an equalized state.

Determination of the barodiffusion coefficient is based on a substitution of capillary barodiffusion for diffusion of water in an external pressure field. It is assumed that on achieving a steady state flow of water through the body, the values of the pressure gradient due to the external pressure field become equalized with the capillary pressure gradient. The overall volume flow of moisture is then given by the expression:

$$h = h_c + h_p, \quad (13)$$

where h_c is the moisture flow due to the moisture gradient and h_p is either the moisture flow due to capillary barodiffusion or that due to an external pressure gradient. In the respective experiment, it is necessary to comply with the condition that both the body and its surface are saturated with water. If the body surface were not saturated with water, the overall volume flow of moisture would be given by the equation:

$$h = h_c + h_{p1} + h_{p2}, \quad (14)$$

where h_{p1} would be the moisture flow due to an external pressure field and h_{p2} would then be the moisture flow due to capillary suction at the non-saturated body surface. The further conditions for the determination of D_p are as follows: (i) attainment of a steady state, i.e. $h = \text{const}$, and the possibility to determine h . (ii) an isothermal medium and experimental maintenance of unidimensional conditions, (iii) determination of P_1 , P_2 and C_1 and C_2 corresponding to conditions (7). On the basis of these conditions the authors designed an apparatus shown schematically in Fig. 1. A cylindrical body 2 cm in diameter and 1 cm in length, prepared by drawing on a vacuum auger, is coated with a lacquer so that the two bases

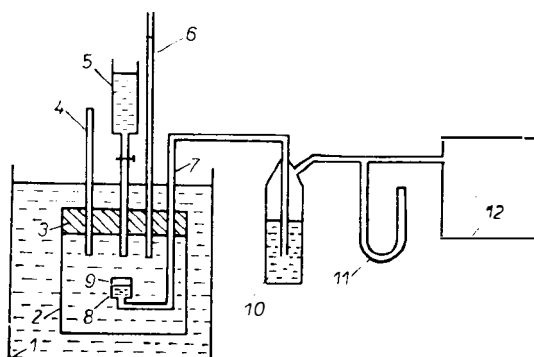


Fig. 1. Schematic diagram of the apparatus for measuring the barodiffusion coefficient of water in a ceramic body; 1 — thermostat, 2 — vessel with water, 3 — stopper, 4 — thermometer, 5 — water stock vessel, 6 — pipette, 7 — glass tube, 8 — frit, 9 — body, 10 — washing bottle, 11 — manometer, 12 — suction pump.

only permit exchange of moisture with the environment. The unidimensionality of moisture transfer is ensured in this way. Fig. 1 shows that one of the bases of body 9 rests on frit 8 and the joined surroundings are insulated with paraffin wax. The entire system is placed in vessel 2 with water kept in thermostat 1. Through stopper 3 of vessel 2, water is supplied from water stock vessel 5 (burette), and there is thermometer 4 and pipette 6 which measures the changes in the volume of water in the system due to sucking the water through the body. The suction is effected by underpressure provided by suction pump 12 via washing vessel 10. The pressure P_2 is read on manometer 11. The piping 7 between the frit and vessel 10 maintains water around the frit, thus keeping it water-saturated and in this way ensuring saturation of one body base surface. Because the body is situated in water, the surface of the other body base is likewise water-saturated so that the experiment conforms to the validity of equation (13). The value of P_1 corresponds

to atmospheric pressure. Following attainment of a steady state, when the volume rate of flow of water \dot{V} has been read, the moisture profile in the body is determined by cutting it in the direction x into slices 2 mm in thickness. The volume moisture contents C_1 and C_2 are then expressed from an approximation of the moisture profile using the linear dependence according to equation (10).

RESULTS

Using the procedure outlined above, the moisture profile was measured in a ceramic mix body with an elevated content of $\alpha\text{-Al}_2\text{O}_3$ at 293 K. The measurement was carried out 10 times. The external pressure value was $P_1 \approx 0.1$ MPa. The volume moisture flow h was calculated from the equation $h = \dot{V}/F$, where F is the surface area of the body base. A typical moisture profile is shown in Fig. 2.

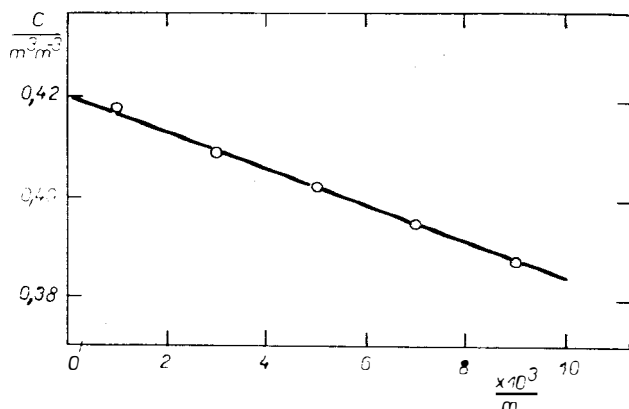


Fig. 2. Distribution of moisture in the body.

Table I

A list of experimental data and calculated values of the barodiffusion coefficients of water

Measurement number	$\frac{P_2}{\text{Pa}}$	$\frac{P}{\text{Pa}}$	$\frac{hx \cdot 10^7}{\text{ms}^{-1}}$	$\frac{C_1}{\text{m}^3 \text{m}^{-3}}$	$\frac{C_2}{\text{m}^3 \text{m}^{-3}}$	$\frac{D_p \cdot 10^{14}}{\text{m}^2 \text{s}^{-1} \text{Pa}^{-1}}$
1	666.6	19 823	1.90	0.4098	0.3780	1.9
2	599.9	19 428	1.68	0.4241	0.3898	1.7
3	666.6	19 823	1.90	0.4185	0.3825	1.9
4	666.6	19 823	1.68	0.4200	0.3848	1.7
5	599.9	19 428	2.63	0.4093	0.3813	2.6
6	666.6	19 823	2.48	0.4115	0.3695	2.5
7	666.6	19 823	1.83	0.4125	0.3896	1.8
8	666.6	19 823	1.75	0.4081	0.3692	1.8
9	666.6	19 823	2.19	0.4105	0.3844	2.2
10	599.9	19 428	1.68	0.4026	0.3802	1.7

The value of the diffusion coefficient D was calculated from its temperature dependence established for the given porcelain mix by the diffusion couple method [3]:

$$D = 5.52 \times 10^{11} \exp(-14484 \text{ K/T}) \text{ m}^2\text{s}^{-1}. \quad (15)$$

The barodiffusion coefficient was calculated according to the equation (8). A survey of the experimental data and calculated values of the barodiffusion coefficient from 10 measurements, related to the mean pressure \bar{P} according to (12) is listed in Table I.

DISCUSSION AND CONCLUSION

The experimental work has shown that in addition to the conditions specified for the method above, the moisture profile in the body has to be determined in the initial stage of the steady state. When the time of measurement is protracted, the ceramic mix at the body base loses its initial cohesion as a result of its free contact with water in the vessel. The process was proved to achieve its steady state within about 1.5 hour. The destruction of the free body surface occurs after 7 hours of measurement. Compliance with the conditions then allows the barodiffusion coefficient of water in a saturated ceramic body in plastic state to be determined reliably by the method suggested. For the water-saturated porcelain mix in question, the mean barodiffusion water coefficient for $T = 293 \text{ K}$ has the value

$$\bar{D}_p = (2.0 \pm 0.3) \times 10^{-14} \text{ m}^2\text{s}^{-1}\text{Pa}^{-1}. \quad (16)$$

A comparison of this value with the value D_p calculated for the same mixture (cf. 1) shows a very satisfactory agreement. This means that when one knows the mean size of the capillaries in the body, equation (4) can be utilized for estimating the barodiffusion coefficient of water in a saturated ceramic mix.

References

- [1] Havrda J., Oujirí F.: *Silikáty* 26, 107 (1982).
- [2] De Groot S. R., Mazur P.: *Non-Equilibrium Thermodynamics*. North Holland, Amsterdam 1962.
- [3] Havrda J., Oujirí F.: *Silikáty* 26, 3, 203 (1982).

BARODIFÚZE VODY V KERAMICKÉ SMĚSI

Jiří Havrda, František Oujirí, Marie Žižková

Katedra technologie silikátů, Vysoká škola chemicko-technologická, 166 28 Praha 6

Na základě znalosti hodnot efektivního difúzního koeficientu, difúzního koeficientu koncentrační difúze, středního poloměru kapilár, povrchového napětí vody a rozdílu objemových vlhkostí ve vodou nasyceném porcelánovém tělese v plastickém stavu je proveden výpočet barodifúzního koeficientu vody. Dále je vypracována metoda měření barodifúzního koeficientu vody, při níž je difúze jednorozměrná. Základem metody je prosávání vody vrstvou zrnitého materiálu. Předpokládá se, že při rovnosti hodnot gradientu tlaku vnějšího tlakového pole a kapilárního tlaku dojde ke vzniku stejného objemového toku vody tělesem. Jsou také určeny podmínky metody pro spolehlivé stanovení barodifúzního koeficientu. Experimentálně je stanovena jeho hodnota ve vodou nasycené porcelánové směsi při teplotě 293 K a provedeno její porovnání s hodnotou vypočtenou.

Obr. 1. Schéma aparatury k měření barodifúzního koeficientu vody v keramickém tělese; 1 — termostat, 2 — nádoba s vodou, 3 — zátka, 4 — teploměr, 5 — zásobník vody, 6 — pipeta, 7 — skleněná trubka, 8 — fritta, 9 — těleso, 10 — promývací láhev, 11 — manometr, 12 — vývěva.

Obr. 2. Rozložení vlhkosti v tělese.

БАРОДИФУЗИЯ ВОДЫ В КЕРАМИЧЕСКОЙ СМЕСИ

Иржи Гаврда, Франтишек Оуиржи, Марие Жижкова

кафедра технологии силикатов, Химико-технологический институт
166 28 Прага

На основании величин эффективного коэффициента диффузии, коэффициента концентрационной диффузии, среднего параметра капилляр, поверхностного натяжения воды и различия объемных влажностей в насыщенном водой фарфоровом теле в пластическом состоянии проводили расчет бародиффузионного коэффициента воды. Далее разрабатывали метод измерения бародиффузионного коэффициента воды, где диффузия одноразмерна. Основой метода является водопроницаемое слоем зернистого материала. Предполагается, что при равенстве величин градиента давления внешнего барического поля и капиллярного давления возникает одинаковое объемное протекание воды телом. Авторами устанавливаются также условия метода для надежного определения бародиффузионного коэффициента. Экспериментальным путем устанавливается его величина в насыщенной водой фарфоровой смеси при температуре 293 К и проводится ее сопоставление с рассчитанной величиной.

Рис. 1. Схема аппаратуры для измерения бародиффузионного коэффициента воды в керамическом теле; 1 — термостат, 2 — сосуд с водой, 3 — пробка, 4 — термометр, 5 — бункер воды, 6 — пипетка, 7 — стеклянная трубка, 8 — фритта, 9 — тело, 10 — промывалка, 11 — манометр, 12 — вакуумный насос.

Рис. 2. Распределение влажности в теле.

STÁLE SE HLEDAJÍ KERAMICKÉ ELEKTROLYTY S PROTONOVOU VODIVOSTÍ.

Velký hospodářský význam by mělo zavedení úsporných metod elektrolýzy vody, jako způsobu skladování přebytečné (zejm. noční) elektrické energie. Jeden z neefektivnějších způsobů je elektrolýza vodní páry při teplotě 250—350 °C v článku, jehož elektrolyt je z keramického iontového vodiče, kde by byl proud přenášen vodíkovými ionty. Vhodné látky, které by měly při dostatečné protonové vodivosti nutnou mechanickou pevnost a životnost aspoň 100 hodin v provozu, se usilovně hledají. Podle citovaného pramene [1] byly zkoušeny γ -AlOOH, α -FeOOH, SbOOH a $H(H_2O)$. β'' alumina (hydronium β'' alumina). Zejména posledně uvedená látka dala nadějně výsledky, její vodivost dosahovala hodnoty $10^{-1} \Omega^{-1} \text{cm}^{-1}$. Nevýhovouje však zatím její životnost, neboť již po krátké době provozu ztrácela pevnost.

[1] Panclor S.: Novel Oxides having high protonic conductivity as electrolyte for low-temperature vapour electrolysis. Rep. EUR 7573N (1981) (Brit. Cer. Abstr. č. 10, str. 210, 3237 (1982)).