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THERMOELECTRIC PROCESS IN WATER-SATURATED CERAMIC MIX

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The method of three thermal sources, based on creation of a constant electric field potential and a temperature profile in the body, was worked out for the purpose of determining the thermoelectric coefficient. The results showed that the effect of the thermoelectric process on the flux of electric current can be neglected.

INTRODUCTION

A water-saturated ceramic mix is regarded as a binary mixture of incompressible components, where the solid phase (the ceramic material) consists of neutral particles homogeneously surrounded with water or electrolyte. On this assumption, the transmission of electric charges can be regarded as diffusion, because it involves a relative movement of ions with respect to neutral particles. From the standpoint of electric current transmission, the water-saturated ceramic mix then behaves as an inhomogeneous electric conductor for which the following equation holds according to the thermodynamics of irreversible processes [1—3]:

$$\mathbf{j} = -\sigma \operatorname{grad} \varphi - L_1 \operatorname{grad} c - L_2 \operatorname{grad} T, \tag{1}$$

where σ is the specific electric conductivity, grad φ is the electric field potential, c is concentration, T is temperature and L_1 and L_2 are phenomenological coefficients. By rearranging equation (1) one obtains:

$$\mathbf{j} = -\sigma(\operatorname{grad} \varphi + (L_1/\sigma) \operatorname{grad} c + (L_2/\sigma) \operatorname{grad} T) \tag{2}$$

and on introducing

$$\mathbf{j} = \sigma \mathbf{E}, \tag{3}$$

where $\mathbf{E}$ is the electric field intensity, for which it holds that $\mathbf{E} = -\operatorname{grad} \varphi$, one obtains

$$\mathbf{j} = \sigma(\mathbf{E} + \mathbf{E}_v), \tag{4}$$

where $\mathbf{E}_v = -(L_1/\sigma) \operatorname{grad} c - (L_2/\sigma) \operatorname{grad} T$ is the imprinted electric field intensity, which specifies the non-electrical causes of electric current. In the given case, it is associated with the concentration gradient and the temperature gradient. The electric current may therefore also arise as a result of the diffusion-electric process, due to the concentration gradient, and as that of the thermoelectric process, due to the temperature gradient. The phenomenological coefficients L_1 and L_2 can therefore be given the terms diffusion-electric coefficient and thermo-electric coefficient respectively. To describe the behaviour of a water-saturated ceramic mix in an electric field it is therefore necessary to determine the significance of the imprinted electric field intensity on current transmission, i.e. to determine the values of coefficients L_1 and L_2.

The present study had the aim to work out a method for reliable determination of the thermoelectric coefficient in a water-saturated porcelain mix and to determine the significance of the effect of the thermoelectric process on the electric current flux.

THE METHOD USED IN DETERMINING THE THERMOELECTRIC COEFFICIENT

During unidirectional transmission of electric current in a prism-shaped body L in length under the condition of zero concentration gradient, an electric field potential and a temperature gradient will develop inside the body. After a certain time, the process will equalize, i.e. j = const., and the electric current flux density is then described by the equation

$$j = -\sigma \, \mathrm{d}\varphi/\mathrm{d}x - L_2 \, \mathrm{d}T/\mathrm{d}x, \tag{5}$$

where x is the ordinate in the direction of the transmission. At the same time, for j it holds that

$$j = -\sigma_{\mathrm{eff}} \, \mathrm{d}\varphi/\mathrm{d}x, \tag{6}$$

where σ_{eff} has the significance of effective specific electric conductivity, also including the effect of the temperature gradient. In a staedy state, the following equation for the calculation of the thermoelectric coefficient is obtained by joining equations (5) and (6):

$$L_2 = (\sigma_{\mathrm{eff}} - \sigma) \, (\mathrm{d}\varphi/\mathrm{d}x) \, (\mathrm{d}T/\mathrm{d}x)^{-1}. \tag{7}$$

In order to calculate the thermoelectric coefficient L_2 in steady state, one has therefore to know σ_{eff}, σ, the electric field potential $\mathrm{d}\varphi/\mathrm{d}x$ and the temperature gradient in the body, $\mathrm{d}T/\mathrm{d}x$.

The relationship for the calculation of $\mathrm{d}T/\mathrm{d}x$ from the temperature profile can be obtained by resolving the transmission equation of heat with an internal three-dimensional source of heat. For unidirectional heat transmission and on the condition that ϱ, c_p, λ = const., it has the form

$$\varrho c_p \, \partial_t T = \lambda \, \partial_x^2 T + \varrho r, \tag{8}$$

where ϱ is the density, c_p is the specific heat, λ is the thermal conductivity, ϱr is the three-dimensional heat source ∂_t and ∂_x represents a derivative in terms of time and the ordinate. For a steady state, i.e. when $\partial_t T = 0$, ϱr = const., equation (8) acquires the form

$$a \, \partial_x^2 T + r c_p^{-1} = 0, \tag{9}$$

where a is the thermal conductivity for which it holds that $a = \lambda/\varrho c_p$. On introducing the designation $K = -r/c_p a$ and resolving equation (9) for the boundary conditions

$$\begin{array}{ll} x = 0, & T = T_1 \\ x = L, & T = T_2 \end{array} \quad T_2 > T_1, \tag{10}$$

we obtain the temperature profile having the form

$$T = Kx^2 + bx + T_1, \tag{11}$$

where $b = (T_2 - T_1)/L - KL$.

To determine L_2 and its temperature dependence, the authors suggested the method of three thermal sources, which ensures unidirectional transmission of electric current and heat. The method is based on creating and determining a constant electric field potential and a temperature profile in the body in steady state, when the heat is supplied by two external sources and one internal source.

The apparatus, whose schematic diagram is shown in Fig. 1, consists of two thermostats *1*, *2*, which supply water at temperatures T_1 and T_2 into copper prisms *3*. A body 30 mm × 30 mm in cross section and L in length, provided with thermal insulation *6* and a moisture barrier 5 is placed between the two thermostats, while it holds that $L \in (48 \text{ mm}; 53 \text{ mm})$. Two electrodes *8* (carbon-filled rubber with aluminium wool) supply the body with constant adjustable alternating voltage from transformer *12*, the voltage being indicated by voltmeter *11*. Another voltmeter *13* measures the voltage on the body. The current passing through the body is recorded by ammeter *10*. The system (heat sources *1*, *2* — electrodes *8* — and body *4*) is loaded by force $F = 6$ N. The temperature field in the body is measured by copper-constantan thermocouples *7*.

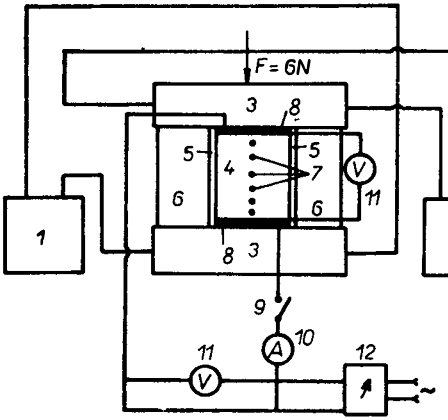

Fig. 1. Schematic diagram of the apparatus for the method of three heat sources; 1, 2 — water thermostats at temperatures T_1 and T_2 3 — copper prisms, 4 — body, 5 — moisture barrier, 6 — thermal insulation, 7 — thermocouples, 8 — electrodes, 9 — switch, 10 — ammeter, 11 — voltmeter, 12 — transformer.

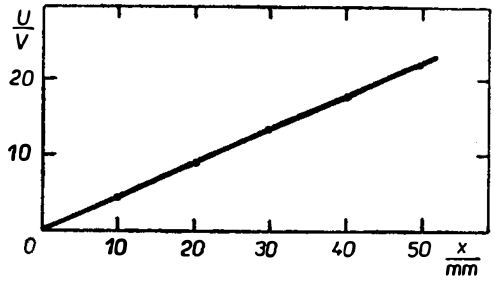

Fig. 2. Relationship $U = U(x)$.

The bodies were prepared from water-saturated porcelain mix with a zero content of soluble salts (grad $c = 0$) [5] with a moisture content of 26 % by forming on an auger. Following moisture-proofing, the bodies were kept for 48 hours in a water-saturated medium at constant temperature. Using the procedure described in [4], the bodies were subjected to unidirectional measurement of electric field potential in the experimental arrangement showed in Fig. 1. For the temperatures $T_1 = 298.1$ K and $T_2 = 320.7$ K and the overall voltage $U = 30$ V, the relationship $U = U(x)$ measured on the body of $L = 4.9\ 10^{-2}$ is plotted in Fig. 2.

The experimental results indicate that at a temperature gradient of 461 Km^{-1} on the body, the voltage on the body amounts to 22 V and the dependence $U = U(x)$ is linear. The voltage on the body corresponds to the electric field potential of $\mathrm{d}\varphi/\mathrm{d}x = 449\ \mathrm{Vm}^{-1}$.

The temperature profiles in the body in steady state were measured under two different conditions, i.e. (i) without connecting, and (ii) after connecting the body into the electric circuit. The results of the measurements for the body voltage $U = 22$ V are shown in Fig. 3. When the body has not been connected to the electric circuit, the temperature profile obtained by resolving equation (9) without the three-dimensional heat source, i.e. $\underset{\sim}{q}r = 0$, for conditions (10) has the form

$$T = (T_2 - T_1)\, x/L + T_1 \tag{12}$$

and for the mean body temperature in holds that

$$\bar{T} = (T_1 + T_2)/2. \tag{13}$$

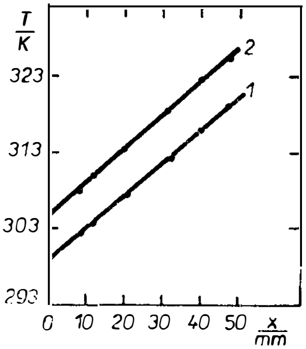

Fig. 3. Temperature profile in the body at U = 22 V; 1 — without electric current, 2 — with electric current.

Approximation of the experimental data (Fig. 3, relationship 1) by means of equation (12) yields the following temperature gradient in the body:

$$(T_2 - T_1)/L = 455\ \mathrm{Km}^{-1}. \tag{14}$$

In the case of measurements with the body connected to the electric circuit, approximation of the experimental data (Fig. 3, dependence 2) by means of equation (11) provides the temperature profile in the form

$$T = (-13.3332x^2 + 455.266x + 304.13)\ \mathrm{K}, \tag{15}$$

which gives the following body surface temperatures:

$$T_1 = 304.13\ \text{K}; \quad T_2 = 326.86\ \text{K}. \tag{16}$$

To estimate $\mathrm{d}T/\mathrm{d}x$, let us now introduce a simplification, assuming a linear profile in the body even during the passage of electric current. On neglecting the first term of equation (15) the temperature profile is obtained in the form

$$T = (455.266x + 304.13)\ \text{K}, \tag{17}$$

and from this the temperatures on the body surface,

$$T_1 = 304.13\ \text{K}; \quad T_2 = 326{,}89\ \text{K} \tag{18}$$

and the temperature gradient in the body,

$$(T_2 - T_1)/L = 455.2\ \text{Km}^{-1}. \tag{19}$$

When taking into account that an inaccurate determination of the position of thermocouples in the body amounting to 0.5 mm corresponds to an error of 0.24 K in the determination of temperature, the simplification introduced into the evaluation of the temperature gradient is justified. Having introduced this assumption one can find by comparing the temperature gradients, with the use of equations (14) and (19), that connection of the body to the voltage will create a linear temperature profile with a slope which is identical to that obtained without the passage of electric current, merely at a higher mean body temperature.

Measurements of the development of the temperature field in the body during passage of electric current in terms of time and similar measurements carried out with the body disconnected from the electric circuit indicated that the heating inside the body does not involve any creation of temperature gradients in directions y and z.

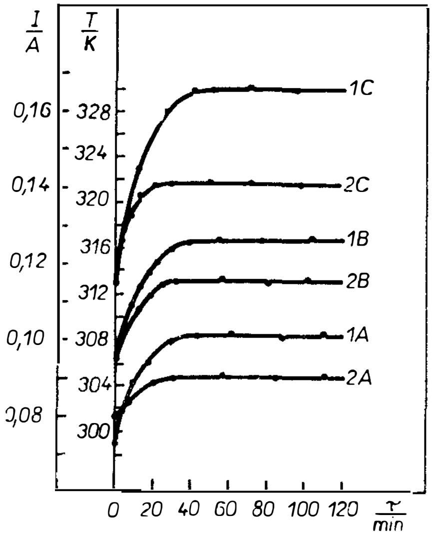

Fig. 4. Time dependence of mean body temperature — 1 and of current — 2

A — $U = 19.5$ V; $\quad \mathrm{d}T/\mathrm{d}x = 291.8\ \text{Km}^{-1}$
B — $U = 22$ V; $\quad \mathrm{d}T/\mathrm{d}x = 474\ \text{Km}^{-1}$
C — $U = 22$ V; $\quad \mathrm{d}T/\mathrm{d}x = 408\ \text{Km}^{-1}$.

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DETERMINATION OF THE THERMOELECTRIC COEFFICIENT BY THE METHOD OF THREE THERMAL SOURCES

The effect of the temperature gradient on electric current transmission in water-saturated porcelain mix was determined experimentally at body voltage $U = 22$ V, or $U = 19.5$ V and at various values of T_1 and T_2. The relationships $I = I(t)$ and $T = T(t)$ were measured, and that of $T = T(x)$ was determined in steady state. Using this procedure, the following relationships for three temperature gradients on the body were established, i.e. 474 $\mathrm{Km^{-1}}$, 408 $\mathrm{Km^{-1}}$ and 291.8 $\mathrm{Km^{-1}}$. The results of the measurements are plotted in Figs. 4 and 5.

With the temperature fields measured, assessment of the justifiability of the simplified evaluation of of $\mathrm{d}T/\mathrm{d}x$ by linearizing these relationships was again assessed. By approximating $T = T(x)$ according to Fig. 5, by means of equation (11) and (12), the temperatures T_1 and T_2 listed in Table I were evaluated. A comparison again indicates a very satisfactory agreement, bearing out correctness of the simplification introduced into the evaluation of the $\mathrm{d}T/\mathrm{d}x$ temperature gradients listed in Table I.

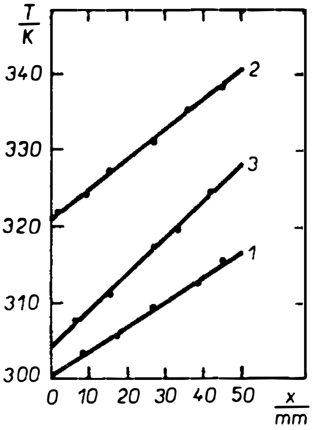

Fig. 5. Temperature profile in the body
1 – $U = 19.5$ V; $\mathrm{d}T/\mathrm{d}x = 291.8$ $\mathrm{Km^{-1}}$
2 – $U = 22$ V; $\mathrm{d}T/\mathrm{d}x = 408$ $\mathrm{Km^{-1}}$
3 – $U = 22$ V; $\mathrm{d}T/\mathrm{d}x = 474$ $\mathrm{Km^{-1}}$.

Table I

Temperatures T_1 and T_2 calculated from temperature profiles by parabolic and linear approximation

	$T = kx^2 + bx + T_1$		$T = (T_2 - T_1)xL^{-1} + T_1$		
U/V	T_1/K	T_2/K	T_1/K	T_2/K	$\mathrm{d}T/\mathrm{d}x$/$\mathrm{Km^{-1}}$
19.5	300.54	316.48	300.48	316.71	291.8
22	320.98	340.59	320.82	340.78	408
22	304.16	328.11	304.12	328.60	474

Table II

The evaluated values in steady state

$\frac{U}{\mathrm{V}}$	$\frac{\mathrm{d}T/\mathrm{d}x}{\mathrm{Km^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{I}{\mathrm{A}}$	$\frac{j}{\mathrm{Am^{-2}}}$	$\frac{\mathrm{d}\varphi/\mathrm{d}x}{\mathrm{Vm^{-1}}}$	$\frac{\sigma_{\mathrm{eff}}}{\mathrm{Sm^{-1}}}$
19.5	291.8	308.6	0.08955	99.50	398	0.250
22	408	330.8	0.1410	156,70	449	0.349
22	474	316.4	0.1152	128.0	449	0.285

The quantities given in Table II were evaluated by means of the data measured in the steady state.

The specific electric conductivity σ for the mean temperatures $\bar{T}$ established and for zero concentration of the soluble salts was calculated from the equation derived in [5] and having the form

$$\sigma = ((0.01678c + 0.0044)\,T - 4.21c - 1.109))\ \mathrm{Sm^{-1}}. \tag{20}$$

The thermoelectric coefficients calculated according to equation (7) are listed in Table III.

Table III

The calculated values of the thermoelectric coefficient

$\frac{\mathrm{d}T/\mathrm{d}x}{\mathrm{Km^{-1}}}$	$\frac{T_i}{\mathrm{K}}$	$\frac{\mathrm{d}\varphi/\mathrm{d}x}{\mathrm{Vm^{-1}}}$	$\frac{\sigma}{\mathrm{Sm^{-1}}}$	$\frac{\sigma_{\mathrm{eff}}}{\mathrm{Sm^{-1}}}$	$\frac{L_2}{\mathrm{AK^{-1}m^{-1}}}$
291.8	308.6	398	0.249	0.250	0.0014
408	330.8	449	0.347	0.349	0.0026
474	316.4	449	0.283	0.285	0.0025

DISCUSSION OF THE RESULTS AND CONCLUSION

The expressed values of thermoelectric coefficients indicate that their values do not depend on the mean body temperature, nor on the temperature gradient value within the intervals of the two quantities actually measured. The mean value of the thermoelectric coefficient is roughly $L_2 = 2 \,.\, 10^{-3}\ \mathrm{AK^{-1}m^{-1}}$. On calculating the share of the two terms on the right-hand side of equation (5) in the electric current flux j from the values listed in Table III, one finds that the thermoelectric term represents approximately 0.6 % of this flux.

If the calculation of L_2 is carried out e.g. with regard to the accuracy of determining the specific electric conductivity σ, one finds that the value of L_2 obtained lies within the tolerance of this accuracy.

On the basis of the measurements performed it may be stated that the method suggested allowed the effect of the thermoelectric process on the alternating current flux in water-saturated porcelain mix to be determined. In resolving technological processes involving an alternating electric internal three-dimensional source of heat, the thermoelectric phenomenon can be neglected.

References

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

[2] Sedov L. I.: *The Mechanics of Continuum* (in Russian), Nauka, Moscow 1976.

[3] Vodák F.: *The Physics of Continuum II* (in Czech), Textbook of Technical University, Prague 1981.

[4] Havrda J., Gregorová E., Oujiří F.: Silikáty *33,* 367 (1989).

[5] Havrda J., Gregorová E., Oujiří F.: Silikáty *33,* 291 (1989).

TERMOELEKTRICKÝ PROCES VE VODOU NASYCENÉ KERAMICKÉ SMĚSI

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Pro kvantitativní popis toku střídavého elektrického proudu ve vodou nasycené porcelánové směsi je nutné znát termoelektrický koeficient a jeho teplotní závislost. Pro jeho stanovení byla vypracována metoda tří tepelných zdrojů, při níž je přenos tepla a proudu jednosměrný. Metoda je založená na vytvoření časově neproměnného elektrického pole a teplotního profilu v tělese. Pro daná napětí byly měřeny časové závislosti proudu a teploty a v ustáleném stavu také teplotní profil. Odtud byly vyhodnoceny termodifúzní koeficienty, které nejsou závislé na střední teplotě tělesa ani na gradientu teploty v proměřených intervalech obou veličin. Vliv termoelektrického procesu na tok střídavého proudu ve vodou nasycené porcelánové směsi lze zanedbat.

Obr. 1. *Schéma aparatury metody tří tepelných zdrojů 1, 2 — termostaty s vodou o teplotě* T_1 *a* T_2, *3 — měděné hranoly, 4 — těleso, 5 — vlhkostní izolace, 6 — tepelná izolace, 7 — termočlánky, 8 — elektrody, 9 — vypínač, 10 — ampérmetr, 11 — voltmetr, 12 — transformátor.*

Obr. 2. *Závislost* $U = U(x)$.

Obr. 3. *Teplotní profil v tělese při* $U = 22$ *V; 1 — bez elektrického proudu, 2 — s elektrickým proudem.*

Obr. 4. *Časová závislost střední teploty tělesa — 1 a proudu — 2*
A — $U = 19{,}5$ V; $\mathrm{d}T/\mathrm{d}x = 291{,}8$ $\mathrm{K\,m^{-1}}$
B — $U = 22$ V; $\mathrm{d}T/\mathrm{d}x = 474$ $\mathrm{K\,m^{-1}}$
C — $U = 22$ V; $\mathrm{d}T/\mathrm{d}x = 408$ $\mathrm{K\,m^{-1}}$.

Obr. 5. *Teplotní profil v tělese*
1 — $U = 19{,}5$ V; $\mathrm{d}T/\mathrm{d}x = 291{,}8$ $\mathrm{K\,m^{-1}}$
2 — $U = 22$ V; $\mathrm{d}T/\mathrm{d}x = 408$ $\mathrm{K\,m^{-1}}$
3 — $U = 22$ V; $\mathrm{d}T/\mathrm{d}x = 474$ $\mathrm{K\,m^{-1}}$.

ТЕРМОЭЛЕКТРИЧЕСКИЙ ПРОЦЕСС В НАСЫЩЕННОЙ ВОДОЙ КЕРАМИЧЕСКОЙ СМЕСИ

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Для количественного описания протока переменного тока в насыщенной водой фарфоровой смеси необходимо знать термоэлектрический коэффициент и его термическую зависимость. Для его установления был разработан метод трех тепловых источников, где перенос тепла и тока протекает в одном направлении. Метод основывается на создании временно непеременного электрического поля и температурного профиля в теле. Для данных намряжений измерялись временные зависимости тока и температуры и в установившемся состоянии также температурный профиль. На основании того исследовали термодиффузионные коэффициенты, которые не зависят от средней температуры тела, ни от градиента температуры в измеряемых интервалах обеих величин. Влиянием термоэлектрического процесса на проток переменного тока в насыщенной водой фарфоровой смеси можно пренебрегать.

Рис. 1. Схема аппаратуры метода трех термических источников; 1, 2 — термостаты с водой температуры T_1 и T_2, 3 — медные призмы, 4 — тело, 5 — влажностная изоляция, 6 — термоизоляция, 8 — электроды, 9 — выключатель, 10 — амперметр, 11 — вольтметр, 12 — трансформатор.

Рис. 2. Зависимость $У = У(x)$.

Рис. 3. Температурный профиль в теле при $У = 22$ V; 1 — без электрического тока 2 — с электрическим током.

Рис. 4. Временная зависимость средней температуры тела — 1 и тока — 2; A — $У = 19,5$ V; $\mathrm{d}T/\mathrm{d}x = 291,8$ км$^{-1}$
B — $У = 22$ V; $\mathrm{d}T/\mathrm{d}x = 474$ Км$^{-1}$
C — $У = 22$ V; $\mathrm{d}T/\mathrm{d}x = 408$ Км$^{-1}$

Рис. 5. Температурный профиль в теле: 1 — $У = 19,5$ V; $\mathrm{d}T/\mathrm{d}x = 291,8$ Км$^{-1}$, 2 — $У = 22$ V; $\mathrm{d}T/\mathrm{d}x = 408$ Км$^{-1}$, 3 — $У = 22$ V; $\mathrm{d}T/\mathrm{d}x = 474$ Км$^{-1}$.

TOVÁRNA NA KERAMICKÉ FILTRY. Americká firma Corning Glass Works postaví poblíž Corning, N. Y. výrobní jednotku, kde bude vyrábět keramické filtry pro čištění roztavených kovů a slitin. Tyto filtry se používají ve slévárnách k odstraňování strusky a nekovových nečistot z tavenin během lití. Corning plánuje přenesení této výroby z jiné keramické továrny do nového provozu, aby čelila stoupající poptávce.

(Am. Ceram. Soc. Bull., *67*, 1988, č. 10. s. 1594)

Doušková

VÝZNAM SKLA V ROCE 2000 byl hlavním tématem jarního zasedání Society of Glass Technology. V oblasti obalového skla by měl být do roku 2000 splněn požadavek na desetinásobně vyšší pevnost a padesátiprocentní snížení hmotnosti, přičemž během příštích dvou let bude stávající pevnost dvoj- až trojnásobně zvýšena. Navíc je nezbytně nutné pro zachování konkurence schopnosti s ostatními obalovými materiály snížit výrobní náklady o 20 %, neboť náklady na vybavení a energii jsou stále příliš vysoké. Další možností snížení nákladů je prodloužení kampaně tavicích pecí až na 15 let, zajištění dalšího snížení počtu pracovních sil pomocí automatizace a výpočetní techniky a omezení ztrát na plnicí lince. Mezi požadavky, kladené na další vývoj sklářských pecí, patří snížení škodlivých emisí, snížení spotřeby energie, zlepšení kvality skla a další využití recyklizace tepla. Poslední typ sklářské pece, testovaný firmou Sorg, využívá rekuperátory pro předehřívání vzduchu. Protože jsou náklady na rekuperátory vyšší ve srovnání s náklady na regenerátory, je odpadní teplo využíváno k předehřívání kmene a střepů. Další výhodou je i to, že předehřívač střepů působí zároveň jako filtr k zachycování emisí. Na zasedání byly dále diskutovány alternativní tavicí metody — především elektrické tavení, využívání barvicích buněk, obohacování spalovacího vzduchu kyslíkem a otápění plazmou. Mnoho z těchto způsobů je dosud ve stádiu vývoje, v některých případech jsou zřejmé problémy s kvalitou utavené skloviny. V oblasti navrhování nových skleněných obalů byl potvrzen přínos systému CAD/CAM. Pomocí tohoto systému je možné nejen určit přesné rozměry skleněného obalu, ale i stanovit jeho přesný objem a vypočítat potřebné množství skloviny. V budoucnu bude systém sloužit ke stanovení výrobních nákladů a ke sledování rozložení napětí.

Glass, *65*, 1988, č. 8, s. 333, 335

Fryntová