DETERMINATION OF THE CONSTITUTIVE EQUATION FOR A CERAMIC PASTE

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A method has been designed which uses the capillary viscometer for determining the constitutive equation for ceramic pastes. The method allows the active forces or pressure at a mean flow velocity or volumetric rate of flow of the paste through the capillary to be measured reproducibly while maintaining the conditions following from the theoretical principle of the method. The results obtained by processing the experimental data are used to describe the flow curve and to derive the constitutive equation for the respective porcelain paste.

INTRODUCTION

Knowledge of the respective form of the constitutive equation is required when a flow model of the non-Newtonian liquid with variable apparent viscosity is to be applied to the resolving of the forming of a ceramic paste. The parameters of this mathematical function are generally obtained by approximating the dependence of apparent viscosity on the shear rate evaluated from the experimentally established functional dependence of shear stress on the shear rate. This dependence can be determined by viscometric measurements, i.e. under the conditions of simple shear flow using various types of viscometers (e.g. rotary or capillary viscometers) [1]. In the case of ceramic pastes, use was made particularly of the Volarovich capillary viscometer method [2], based on measuring the mean flow velocity $\bar{v}_x$ or the volumetric rate of flow $\dot{V}$ of the paste through the capillary while simultaneously measuring the acting force F or the pressure p. The processing of the relationship obtained, $F = f(\bar{v}_x)$, or $p = f(\bar{v}_x)$ is based on resolving the flow of a non-Newtonian liquid through a pipe R in diameter and L in length while assuming that the paste flow velocity at the pipe wall, v_s, is known ($v_s = 0$, or $v_s \neq 0$). Assuming that the ceramic paste can be regarded as an isotropic and incompressible liquid and its flow through the capillary as steady-state and laminar, the following equation for volumetric rate of flow is obtained for isothermal conditions by resolving the generalized Navier—Stokes equation [3]:

$$\gamma_a/\tau_s = \gamma_a\beta/\bar{v}_x + 4\tau_s^{-4} \int_0^{\tau_s} \tau_{rx}^2 \, f(\tau_{rx}) \, \mathrm{d}\tau_{rx},\tag{1}$$

where for γ_a it holds that

$$\gamma_a = 4\bar{v}_x/R,\tag{2}$$

for the shear coefficient β it holds that

$$\beta = v_s/\tau_s,\tag{3}$$

for shear stress at the pipe wall, τ_s it holds that

$$\tau_s = R \, \Delta p/2L\tag{4}$$

and $f(\tau_{rx})$ is the inversion function for the constitutive equation:

$$\gamma(r) = f(\tau_{rx}), \tag{5}$$

where $\gamma(r)$ is the shear rate:

$$\gamma(r) = dv_x/dr. \tag{6}$$

If the flow velocity at the pipe wall is zero, i.e. $v_s = 0$, equation (1) acquires the form:

$$\dot{V}/\pi R^3 = \tau_s^{-3} \int_0^{\tau_s} \tau_{rx}^2 \, f(\tau_{rx}) \, d\tau_{rx}, \tag{7}$$

where $\dot{V}$ is the volumetric rate of flow through the pipe.

The flow behaviour of various liquids can only be compared under identical conditions. This requirement is met at the capillary wall. On relating the quantities being measured to the capillary wall, the experimental data can be expressed in the following form:

$$\Delta p R/2L = f(4\bar{v}_x/R), \text{ or } \tau_s = f(\gamma_a). \tag{8}$$

The processing of experimental data for plotting the constitutive equation is based on rearrangement of equation (7) following introduction of equation (2):

$$(3\gamma_a/4) + (D \, \Delta p/4L) \, d(\gamma_a/4)/d(D \, \Delta p/4L) = f(\tau_s), \tag{9}$$

where D is the capillary diameter. In agreement with equations (4), (5), (6) it also holds that

$$\gamma_s = f(\tau_s) = -(dv_x/dr)_s, \tag{10}$$

where γ_s or $(dv_s/dr)_s$ is the shear rate at the capillary wall. On introducing

$$n' = d \ln \tau_s/d \ln \gamma_a \text{ or } \tau_s = K' \, \gamma_a^{n'}, \tag{11}$$

resolving equations (9), (10), (11) and substituting into (9) one obtains

$$\gamma_s = (3n' + 1) \, \gamma_a/4n'. \tag{12}$$

Equation (12) allows the experimentally established γ_a in equation (8) to be converted to γ_s, the relationship $\eta = f(S)$ to be plotted and the constitutive equation in the form $\tau_s = f(\gamma_s)$ to be evaluated, while the following holds for apparent viscosity:

$$\eta = \tau_s/\gamma_s, \tag{13}$$

and for S:

$$S = \gamma_s^2. \tag{14}$$

Mathematical expression of the constitutive equation is obtained by approximating the graphic plot with the use of a suitable function.

PRECISIONING THE EXPERIMENT ON THEORETICAL BASIS

Equation (11) has been derived for lamiar steady flow under isothermal conditions and on the assumption that $v_s = 0$. These conditions have to be conformed to over the entire range of the relationship (8) being measured.

Laminarity of the flow can be assessed according to the value of the generalized Reynolds criterion in the form [1, 4]:

$$Re_{gen} = D^{n'} \, v_x^{(2-n')} \, \varrho / K' 8^{n'-1},$$
$$\tag{15}$$

where for flow through pipe it holds that

$$Re_{gen} \leqq 2100.$$
$$\tag{16}$$

Equation (1) indicates that for $v_s = 0$, γ_a is an explicit function of τ_s, i.e. if the relationship $\tau_s = f(\gamma_a)$ is measured on capillaries of various diameters, the curves obtained coincide [6]. In other words, a set of curves obtained gives evidence for the presence of shear at the capillary wall. In the given situation, the volumetric flow rate free of a shear layer is given by equation [1]

$$\dot{V} = \dot{V}_{measured} - \beta \tau_s \, \pi R^2,$$
$$\tag{17}$$

where $\tau_s = D \, \Delta p / 4L$ corresponds to $\dot{V}_{measured}$ and β is given by equation (1), or (3). There are other procedures that can be employed to calculate v_s or the correction factors for wall shear, or to calculate the shear layer [1, 6, 7]. According to [5, 7, 8], in the case of very viscous liquids, the shear at the capillary wall can be eliminated by roughening the inner surface, thus preventing the liquid from sliding along the wall.

Attainment of a steady fully developed flow is also affected by the length of the capillary in view of the entry and discharge effects. During entry of the liquid into the capillary the velocity profile is developed gradually and the distance over which it attains the final steady-state shape is called the entry length L_e [1, 5]. The thickness of the boundary layer changes simultaneously [1, 5, 9]. The entry effects are said to be due [1, 5, 10] (i) to conversion of potential energy to the kinetic one in consequence of the change in flow velocity, (ii) to excessive friction of the liquid brought about by the great velocity gradient close to the capillary wall. Calculation of the entry length was dealt with by a number of authors [9, 10, 11, 12]. It generally holds that the value of L_e depends on v_x, D and the value of the Reynolds criterion, and the entry length of Newtonian liquids is described by the equation [1, 5, 10]:

$$L_e = 0{,}0575D \, Re.$$
$$\tag{18}$$

In addition to studies precisioning the numerical factor of equation (18) for non-Newtonian liquids [11, 12], there are also results pointing out the small difference of the correction factor with respect to Newtonian liquids [1, 5, 10].

The discharge effects manifest themselves by an increase in pressure drop Δp compared to the Δp corresponding to steady—state flow. They are caused by the relaxation of axial and radial normal stresses. From the standpoint of rheology, the effect is a result of reversible elastic deformation caused by liquid flow through the capillary [1, 5, 10]. Compared to the entry effects, its influence is much smaller and can be neglected at adequately large L/D ratios [1, 7, 10, 14, 15].

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THE CAPILLARY VISCOMETER METHOD

An analysis of the findings surveyed above allows the requirements of theory on experimental arrangement of the capillary viscometer method to be summarized into the following points:

a) attainment of steady-state fully developed laminar flow of the paste through the capillary under isothermal conditions,

b) possible correction for the end effects,

c) possible determination of shear velocity at the capillary wall.

These requirements, precisioned by theory, have led to the design of the capillary viscometer shown in Fig. 1. The viscometer makes use of replaceable capillaries
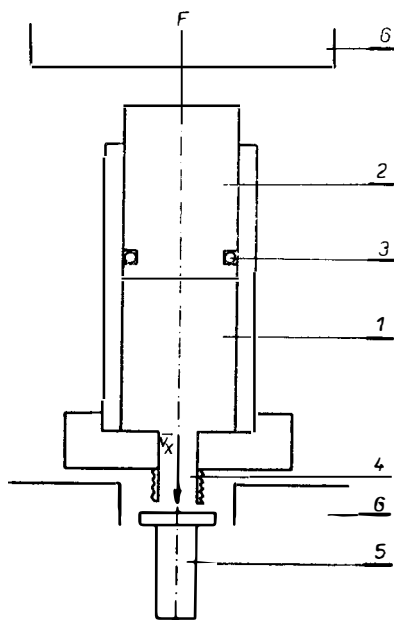

Fig. 1. Schematic diagram of the capillary viscometer; 1 — chamber, 2 — piston, 3 — sealing rings, 4 — chamber mouth, 5 — capillary, 6 — jaws of instrument for mechanical testing.

with an internal thread and the dimensions listed in Table I. The viscometer, in combination with an instrument for measuring the mechanical properties and provided with stepless control of the jaw displacement speed, is able to measure force F required for attaining a preset average flow velocity $\bar{v}_x$ of the paste through

Table I

Dimensions of the capillaries

$D\ 10^3/m$	2.4		3.3		4.2					6.9		
$L\ 10^2/m$	4	8	4	8	4	5	8	10	12	4	5	8

the capillary. The constant character of velocity $\bar{v}_x$ during the measurement, jointly with an adequate amount of the paste in the chamber and with the selectable capillary length allow a steady-state fully developed laminar flow of the paste through the capillary to be attained. Measurement of the initial paste temperature and that after discharge from the capillary serves as a check of maintaining the isothermal conditions.

Measurements with capillaries of various lengths and with a constant diameter were utilized in order to introduce corrections for the end effects and for friction in the chamber. The experimentally established relationship $p = f(\bar{v}_x)$ for two or more capillary lengths made it possible to determine $\Delta p = p_{L1} - p_{L2}$, where Δp is the pressure drop without the end effects over the capillary length $\Delta L = L_1 - L_2$.

The effect of the internal thread in the capillary on the elimination of slip velocity at the wall, v_s, was verified for porcelain paste with a moisture content of 26.1 % by measuring on capillaries of various diameters and a constant length. The resulting relationship $\tau_s = f(4\bar{v}_x/R)$, plotted in Fig. 2, indicates that $v_s = 0$, as the relationships obtained for various capillary diameters are identical.
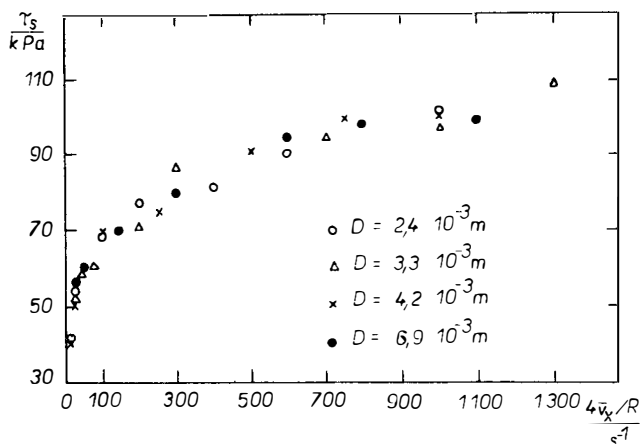

Fig. 2. Relationship $\tau_s = f(4\bar{v}_x/R)$ of porcelain paste for various capillary diameters and a constant capillary length.

The reproducibility of the measurements of basic quantities was evaluated by measurements repeated 5 times on one porcelain paste. The results are summarized in Table II.

Following experimental verification of the requirements on the capillary viscometer, the basic parameters of the porcelain paste were determined in order to formulate its constitutive equation. The graphic interpretation of the rheological behaviour of porcelain paste, measured on capillaries $D_1 = D_2 = 3.3 \times 10^{-3}$ m and $L_1 = 8 \times 10^{-2}$ m, $L_2 = 4 \times 10^{-2}$ m, is shown in Figs. 3 and 4. The graphic plot of the constitutive equation in Fig. 5 was approximated by the equation

$$\tau_s = \tau_0 + K \, (dv_x/dr)_n^s, \tag{19}$$

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Table II

Reproducibility of measurement of the basic quantities

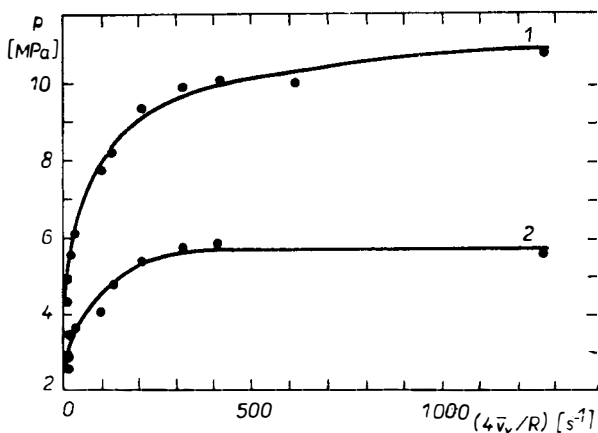| Piston movement velocity $\bar{v}\ 10^4$/m s^{-1}	Force measured F/N
0.07	7,250 ± 16.32
0.16	7,800 ± 12.64
0.56	11,000 ± 12.40
1.73	13,700 ± 12.70
2.78	14,400 ± 13.50
3.70	15,200 ± 9.20
5.11	15,500 ± 13.90
7.41	16,000 ± 13.20

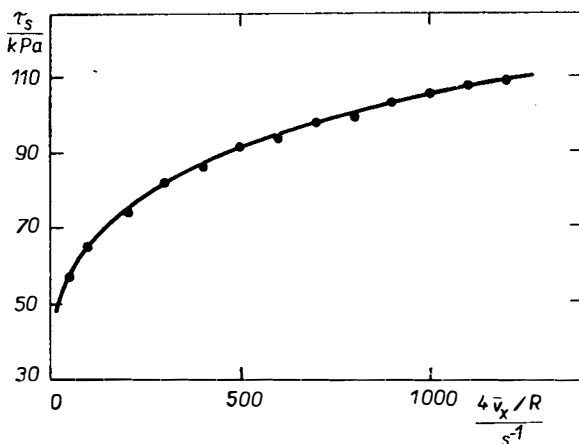*Fig. 3. Relationship $p = f(4\bar{v}_x/R)$ for porcelain paste.*

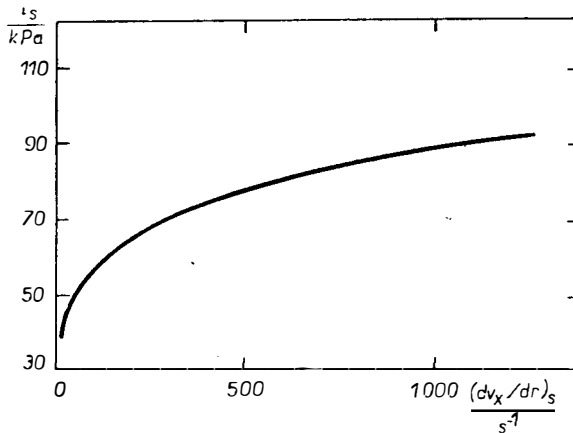*Fig. 4. Relationship $\tau_s = f(4\bar{v}_x/R)$ for porcelain paste.*

Fig. 5. *Relationship* $\tau_s = f(\mathrm{d}v_x/\mathrm{d}r_s)$ *for porcelain paste.*

where the constants had the following values:

$$\tau_0 = 15.7 \,\text{kPa}, \; K = 13.9 \,\text{kPa}\; s^n, n = 0.24. \qquad (20)$$

From equations (15) and (18) it follows that the value of Reynolds criterion over the interval $Re_{gen} \in \langle 1.23 \times 10^{-6}; \; 4.77 \times 10^{-2}\rangle$, and the stabilizing length $L_e \in \langle 8.2 \times 10^{-11}; \; 3.2 \times 10^{-6}\rangle$. This means that the measurement proceeded under the conditions of steady-state fully developed laminar flow of the paste through the capillary.

CONCLUSION

The results of the experimental work allow the findings obtained to be summarized into the following points:

(i) the suggested simple capillary viscometer method is suitable for reproducible measurement of the initial parameters required for evaluating the constitutive equation of the respective liquid while conforming to the conditions following from the theoretical principle of the method,

(ii) the procedure employed in the processing of the experimental data allowed the flow curve and the constitutive equation of porcelain paste to be expressed in the form of equation (19) where the constants had the values given in (20).

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STANOVENÍ KONSTITUTIVNÍ ROVNICE KERAMICKÉ PASTY

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Je vypracována metoda kapilárního viskozimetru pro stanovení konstitutivní rovnice keramické pasty. Princip metody spočívá v měření působící síly, resp. tlaku při předem známé střední rychlosti toku, resp. objemového průtoku pasty kapilárou. Reprodukovatelné měření výchozích dat je umožněno při současném dodržení podmínek plynoucích z teoretického základu metody. Aplikovaný postup zpracování experimentálních dat umožnil vyjádření tokové křivky, funkční závislosti viskozity na gradientu rychlosti deformace a následné vyhodnocení konstitutivní rovnice porcelánové pasty. Znalost konstitutivní rovnice dovoluje řešit matematický model toku dané keramické pasty trubkou popisující rychlostní poměry v ústí lisu při jejím tvarování.

Obr. 1. Schéma kapilárního viskozimetru; 1 — zásobník, 2 — píst, 3 — těsnicí kroužky, 4 — ústí zásobníku, 5 — kapilára, 6 — čelisti zařízení pro měření mechanických vlastností.
Obr. 2. Závislost $\tau_s = f(4\bar{v}_x/R)$ porcelánové pasty pro různé průměry kapilár s konstantní délkou.
Obr. 3. Závislost $p = f(4\bar{v}_x/R)$ pro porcelánovou pastu.
Obr. 4. Závislost $\tau_s = f(4\bar{v}_x/R)$ pro porcelánovou pastu.
Obr. 5. Závislost $\tau_s = f(dv_x/dr)_s$ pro porcelánovou pastu.

ОПРЕДЕЛЕНИЕ КОНСТИТУТИВНОГО УРАВНЕНИЯ КЕРАМИЧЕСКОЙ ПАСТЫ

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Был разработан метод капилярного вискозиметра, предназначенногс для определения конститутивного уравнения керамической пасты. Принцип метода заключается в измерении действующей силы или давления при заранее известной средней скорости течения или объемного протока пасты через капиляр. Возможность воспроизводимого измерения исходных данных заключается в одновременном соблюдении условий, вытекающих из теоретической сущности метода. Применяемый метод обработки экспериментальных данных предоставляет возможность установить кривую протока, функциональную зависимость вязкости от градиента скорости деформации и последовательную оценку конститутивного уравнения фарфоровой пасты. Зная конститутивное уравнение, можно решать математическую модель протока данной керамической пасты через трубку, описывающую соотношения скоростей в мундштуке пресса при ее формировке.

Рис. 1. Схема капилярного вискозиметра; 1 — бункер, 2 — поршень, 3 — прокладочные кольца, 4 — устье бункера, 5 — капиляр, 6 — челюсти установки для измерения механических свойств.
Рис. 2. Зависимость $\tau_s = f(4\bar{v}_x/R)$ фарфоровой пасты для разного размера капиляр с постоянной длиной.
Рис. 3. Зависимость $p = f(4\bar{v}_x/R)$ для фарфоровой пасты.
Рис. 4. Зависимость $\tau_s = f(4\bar{v}_x/R)$ для фарфоровой пасты.
Рис. 5. Зависимость $\tau_s = f(dv_x/dr)_s$ для фарфоровой пасты.