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Rheological and Casting Properties of a Porcelain Mixture

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Abstract: A mathematical model has been presented to describe the influence of the solids and electrolytes concentration on the rheological and casting properties of porcelain slips and on the bending dry strength of castings.

The shear-dependent behaviour of the casting slips is pseudoplastic with an expressed yield stress, and the Herschel–Bulkley equation provided the best data fitting for the flow curves. A pronounced thixotropy is also established.

The rheological parameters and casting rate decrease by reducing the solids concentration and increasing the amount of sodium silicate in the slips. Optimal values areas of the solids and sodium silicate concentration for each composition of the solid phase with respect to the rheological and casting properties of slips, as well as the bending dry strength of castings are determined. The correlation dependences between the mechanical, casting and rheological properties are thus obtained.

1 INTRODUCTION

The knowledge of the rheological properties of whiteware suspensions is of paramount importance in the ceramic industry for improving the production processes and quality of the manufactured wares.

For a known solid phase, the rheological behaviour of the casting slips is mainly influenced by the solids concentration and the kind and amount of the electrolytes. It is of great practical importance to ensure the most appropriate combination of these quantities for optimal slip-casting. For whiteware suspensions the complexity of the dispersed phases (different types of clays and non-plastic materials) complicates the relation between the solids concentration and the suspension properties, depending on the activity, the surface area and the hydrofility of the components.

Investigations of the influences of the solids and electrolytes concentration on the rheological behaviour of clay–kaolin aqueous suspensions[1-5] and of porcelain slips[6-10] have been reported. More attention has been given to the type and amount of the electrolytes. The relation between these factors and the rheological coefficients in the models describing the rheological behaviour of the systems has been less well studied.

The present work is directed towards studying the rheological and casting characteristics of porcelain casting slips and determining the optimal values of solids and electrolytes concentration with respect to the rheology and technology of slip-cast porcelain. This will help in facilitating and optimizing the slip-casting process and in improving the quality of the products.

2 EXPERIMENTAL

2.1 Materials

The following Bulgarian raw materials were used: processed kaolins V_1 and D_1, alkaline pegmatite and quartz sand. The non-plastic materials were ball-milled separately.

Porcelain casting slips were prepared by mixing in a beaker the necessary amount of distilled water and a fixed amount of solid phase added to give the required solid–water concentration on a

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mass basis. The electrolytes were preliminarily added to the distilled water: 0·1% (wt) sodium carbonate for all slips and sodium silicate (silica modul 2·6), which was varied in the range (0·1–0·3%) (wt). After sufficient stirring the slips were screened through a 100-μm mesh sieve and stored for 24 h in a sealed plastic container before testing.

Several specimens with dimensions 10 × 18 × 150 mm were cast in laboratory plaster moulds and dried at 110°C for determining the bending dry strength.

2.2 Experimental methods

The rheological measurements were carried out with a rotational viscosimeter*, a cylindrical system S/S1 in the range of shear rates $\dot{\gamma}$ = 0–1312 s^{-1}. All tests were performed at a temperature of 20°C. The flow curves were obtained by increasing and decreasing the shear rate.

The casting rate (C_H) was defined using plaster cylinders with dimensions l = 30 mm, d = 15 mm and calculated by means of the following equation:[11]

$$C_H = \frac{m}{F \cdot t}, \ \text{g/cm}^2\cdot\text{s} \qquad (1)$$

where m is the separated dry substance, g; F — the area of the immersed plaster cylinder in the slip, cm^2; t — the time of stay in the casting slip, 300 s.

The bending dry strength of the casting specimens was measured by means of a bending strength tester.†

The investigated factors were varied in the intervals: clay constituent content X_1 = 0·40–B_1, quartz content X_2 = 0·14–0·33, feldspar content X_3 = 0·15–0·34, solids concentration X_4 = 65–69% (wt), sodium silicate concentration X_5 = 0·1–0·3% (wt). The factors X_1, X_2, X_3 are the components in the rational composition of the porcelain mixture and condition $\sum_{i=1}^{3} X_i = 1$ is fulfilled. The dependence of the upper limit of factor X_1 on the factors X_4 and X_5 is established. It is described by the following regression equation:

$$B_1 = X_1^{\max} = -9{\cdot}02 + 0{\cdot}29X_4 + 0{\cdot}31X_5 - 0{\cdot}23{\cdot}10^{-2}\, X_4^2 \qquad (2)$$

In order to obtain this dependence the maximum time $t \leq 75$ s for flowing out of the casting slips from a single-point measuring viscosimeter was assumed.

The following quality indices were chosen: Y_1 is the yield stress, τ_o Pa; Y_2 — the apparent viscosity at $\dot{\gamma}$ = 81 s^{-1}, η_{81} mPa·s; Y_3 — the area of the hysteresis loop, A mm^2; Y_4 — the casting rate, C_H g/cm^2·s; Y_s — the bending dry strength of the specimens, S_d MPa.

3 RESULTS AND DISCUSSION

Some flow curves of the investigated casting slips for a porcelain mixture with rational composition:clay constituent X_1 = 0·40, quartz X_2 = 0·33 and feldspar X_3 = 0·27 and with different solids and electrolytes concentration are shown in Fig. 1.

The rheological behaviour of the investigated casting slips is most precisely described by the Herschel–Bulkley equation in the whole investigated area.[12] From the calculated flow indices values and from the curves (Fig. 1), it is evident that the slips demonstrate pseudoplastic behaviour (n < 1) with an expressed yield stress. Time-dependent behaviour or a pronounced thixotropy is also established.

The experimental data were gathered and processed according to a D-optimal plan to construct regression models of the indices (Y_k) of the type:[12]

$$Y_k = \sum_{i=1}^{q} b_i X_i + \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} b_{ij} X_i X_j + \sum_{i=q+r}^{m} b_{ii} X_i^2, \qquad (3)$$

where: q = 3, i = 1, 2, 3; r = 2, j = 4, 5; m = q + r, k = 1–5.

The dependence of the rheological and casting properties of porcelain casting slips and the mechanical properties of intermediate products on the solids and electrolytes concentration are graphically shown in Figs 2–4 for porcelain mixture composition: clay constituent X_1 = 0·45;

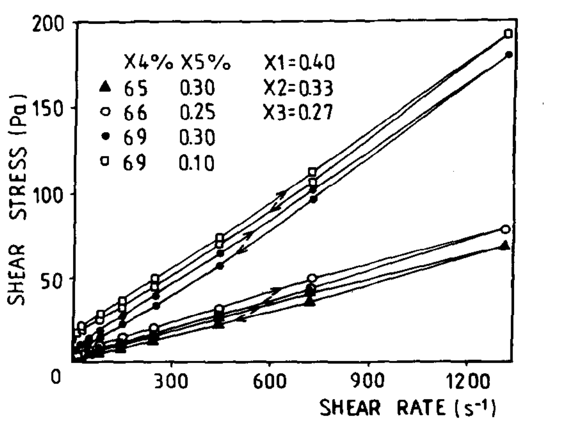

Fig. 1. Flow curves of porcelain casting slips for different solids and sodium silicate concentration.

* Viscosimeter type 'RHEOTEST 2·1', Germany.
† Bending strength tester type 'NETZSCH 401/3', Germany.

quartz $X_2 = 0{\cdot}29$; feldspar $X_3 = 0{\cdot}26$. The given rational composition of porcelain mixture was found to be optimal with respect to the rheological and mechanical properties.[12]

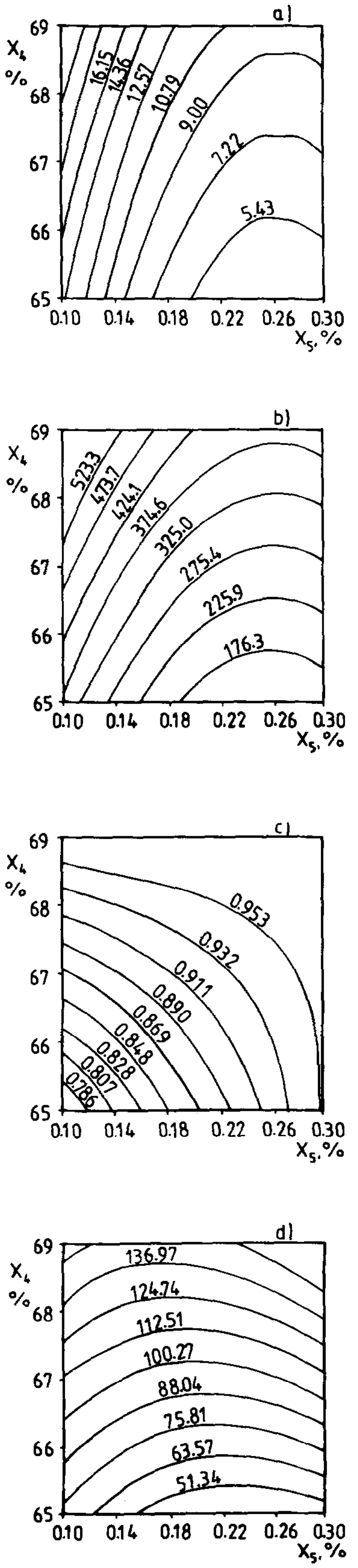

Fig. 2. Dependence of the rheological properties on the solids and sodium silicate concentration: (a) yield stress τ_o, Pa; (b) apparent viscosity η_{81}, mPa·s; (c) flow index n; (d) hysteresis loop area $A \cdot 10^2$, mm^2.

The variation of the yield stress τ_o and the apparent viscosity η_{81} are shown in Fig. 2(a,b), respectively. The yield stress and viscosity decrease by reducing the solids concentration and increasing the amount of sodium silicate. The variation of the hysteresis loop area is similar to Fig. 2(d). It has to be mentioned that the solids concentration exerts a greater influence on the hysteresis loop area than the electrolytes concentration, while the influence of these factors on the yield stress and on the viscosity is nearly equivalent. A tendency for reduction of the influence of solids concentration in the area of higher sodium silicate concentrations ($X_5 \geq 0{\cdot}20\%$) on the yield stress and apparent viscosity is observed.

The decrease of the rheological parameters with lowered solids concentration and increase of the sodium silicate amount is mainly due to the reduced number of particle–particle interactions, the increased zeta potential, and hence the repulsive forces between the particles.

Figure 2(c) shows the effect of solids and sodium silicate concentration on the flow index. This rheological parameter increases with rising solids and electrolytes concentration, which is also expected since the particle–particle interaction determines the slip rheology.

The optimal values for the amount of sodium silicate in relation to the apparent viscosity for each solids concentration are obtained (Fig. 2(b)).

Optimal values for the sodium silicate concentration are also established in relation to the variation of the casting rate (Fig. 3). The casting rate decreases with lowered solids concentration and increased sodium silicate. Undeflocculated casting slips with an excess of electrolyte have a higher casting rate if compared with optimal deflocculated slips. This proves that deflocculation of the casting slips is one of the dominating factors controlling the casting rate, The reduction of the casting rate by increasing the sodium silicate amount is not great — approximately 18%, a fact established also by Basnett and Cartwright.[13]

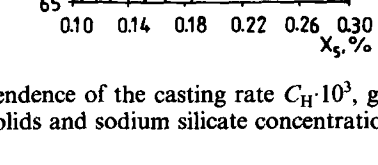

Fig. 3. Dependence of the casting rate $C_H \cdot 10^3$, g/cm^2·s on the solids and sodium silicate concentration.

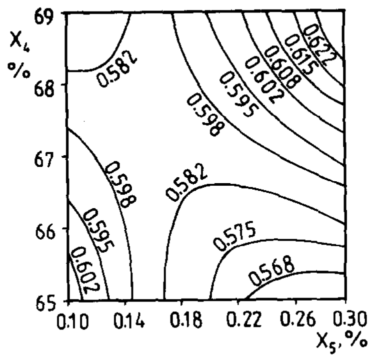

Fig. 4. Dependence of the bending dry strength S_d, MPa on the solids and sodium silicate concentration.

The variation of the bending dry strength of the cast specimens is shown in Fig. 4. The bending dry strength grows by increasing the solids and electrolyte concentration in the range X_4 = 67–69%, X_5 = 0·15–0·30%. This tendency is observed in the whole variation range for the factors by the greater content of clay constituent in the rational composition of porcelain.

It is known from practice that castings with maximum density and bending dry strength can be obtained from slips with maximum fluidity. The optimal deflocculation of the slips guarantees good casting properties and prevents orientated structures which cause anisotropic drying shrinkage, defects and lower bending dry strength.

The results of the present investigation showed that for optimal deflocculated slips the solids and sodium silicate concentration can be varied in the intervals X_4 = 65–67% (wt) and X_5 = 0·18–0·30% (wt), respectively. In this area casting slips with yield stress $\tau_o \leq 7$ Pa, apparent viscosity $\eta_{81} \leq 250$ mPa·s and index of flow $n \geq 0{\cdot}86$, as well as castings with bending dry strength $S_d \geq 0{\cdot}58$ MPa can be obtained.

On the basis of the established relationships of variation of the rheological, casting and mechanical properties, correlation dependences between the casting rate, bending dry strength and parameters yield stress and apparent viscosity are also obtained:

$$C_H = 1{\cdot}84 + 0{\cdot}048 \cdot \tau_0 - 0{\cdot}47 \cdot 10^{-3} \cdot \tau_0^2 \quad (4)$$

$$C_H = 1{\cdot}66 + 2{\cdot}67 \cdot 10^{-3} \cdot \eta_{81} - 1{\cdot}78 \cdot 10^{-6} \cdot \eta_{81}^2 \quad (5)$$

$$S_d = 0{\cdot}45 + 0{\cdot}035 \cdot \tau_0 - 0{\cdot}15 \cdot 10^{-2} \cdot \tau_0^2 \quad (6)$$

$$S_d = 0{\cdot}42 + 1{\cdot}21 \cdot 10^{-3} \cdot \eta_{81} - 1{\cdot}57 \cdot 10^{-6} \cdot \eta_{81}^2 \quad (7)$$

Although the present study is confined to the more fundamental aspects of the behaviour of porcelain slips, the significance of its results are of practical importance, as they indicate the means for making the most suitable casting slip.

4 CONCLUSIONS

From the performed investigation, the following conclusions can be derived:

(1) Decreased solids concentration and the increased electrolytes concentration reduce the rheological parameters (yield stress, apparent viscosity, hysteresis loop area) and the casting rate.
(2) Optimal values of the sodium silicate concentration for each value of the solids concentration and for each solids composition with respect to optimal deflocculated slips are fixed.
(3) Mathematical models offer possibilities for prognosticating the influence of the solids and electrolytes concentration on the rheological and casting properties of porcelain slips and on the bending dry strength of cast products. This can facilitate the control of the wet-shaping process.
(4) The correlation dependences between the casting, mechanical and rheological properties are determined, which can be used for predicting the casting and mechanical properties of porcelain mixtures from the rheological properties of the slips.

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