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HIGH-TEMPERATURE MODIFICATION OF THE TECHNOLOGICAL PROPERTIES OF STONEWARE CLAYS WITH ACTIVE ADDITIVES

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Abstract. The paper presents the results of high-temperature modification of stoneware clays from Łęknica with fly-ash from the Turów power plant and phonolite from Opolno Zdrój. The technique of the design of experiments was adopted. It was assumed that the mathematical characteristic of the object of studies can be approximated by a non-linear regression function of the second order. This function was calculated by the method of regression analysis, using an ODRA 1304 computer. The relationships were determined between the selected physico-mechanical properties of burnt clays and the content of mullite, quartz, cristobalite and glass, and the batch constituents and firing temperature. The resulting regression equations were interpreted graphically. It appears that the rise in burning temperature is attended by an increase in mullite and glass content and a deterioration in compressive strength due to the stresses generated at the crystalline phase — glass boundary. It is the increase in mullite content rather than the higher glass content that lowers the strength of ware. High glass content and high apparent density increase the strength of ware. Optimum batch composition and firing temperature were determined in order to obtain the ware with a compact texture. Bodies with best technological properties, meeting the specifications for high-quality acid-proof stoneware, were obtained from mixes consisting of clay modified with phonolite (20—40%) or fly-ash (30%) and phonolite (40%).

INTRODUCTION

The physico-chemical properties of clays depend on the kind and amount of the constituent clay minerals and non-clay components (quartz, carbonates, iron minerals, sometimes feldspars). It is the latter minerals that determine the utility of clays for the manufacture of ceramic ware of various kinds.

Clay minerals, especially smectites, impart plasticity and strength to clays in the dry state and after burning. They are also responsible for drying and burning shrinkage which will cause the deformation and cracking of ware if a certain limit is exceeded. This property of clays, however, can be controlled by an addition of sand. To increase the plasticity of clays, surface active substances (polyelectrolytes), urea, polyphosphates and other components are added.

In the manufacture of ceramic ware it is imperative that clays should have a required phase composition and texture after firing at a specified temperature. The

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Table 1

The chemical composition of clay (Irena mine at Łęknica), fly-ash (Turów power plant) and trachytic phonolite (Opolno Zdrój)

Chemical composition wt. %	Plastic clay Łęknica		Fly-ash (Turów power plant)	Phonolite (Opolno Zdrój)
	untreated sample	< 0.5 μm fraction		
loss of ignition	10.18	13.80	4.55	2.71
SiO ₂	53.70	45.00	50.93	60.45
Al ₂ O ₃	29.10	34.90	33.85	20.29
TiO ₂	2.32	2.34	0.75	0.10
Fe ₂ O ₃	2.05	2.59	4.23	3.76
CaO	0.12	0.12	1.51	0.55
MgO	0.39	0.28	1.24	0.27
K ₂ O	1.71	0.69	2.10	5.90
Na ₂ O	0.10	0.07	0.85	6.30

Analyses were made at the Institute of Refractories, Gliwice.

The phase composition of clays was modified with fly-ash from the Turów power plant and trachytic phonolite from Opolno Zdrój. Their chemical constitution is given in Table 1. All the chemical analyses were made at the Institute of Refractories in Gliwice.

It is generally known that fly-ash consists of spheroidal aggregates (micro-spheres) made up of mullitized glass, irregular fragments of burnt clay, grains of incompletely burnt coal, quartz and iron oxides.

Phonolite samples were collected from an abandoned quarry in Opolno Zdrój. Two varieties of this rock, differing in their macroscopic features, were distinguished: dark-grey compact rock with light feldspar phenocrysts, and weathered, friable variety of a light-grey colour with weathered cream-yellow feldspar phenocrysts. According to Kozłowski and Skiba-Wyderko (1966), the body of rock is made up

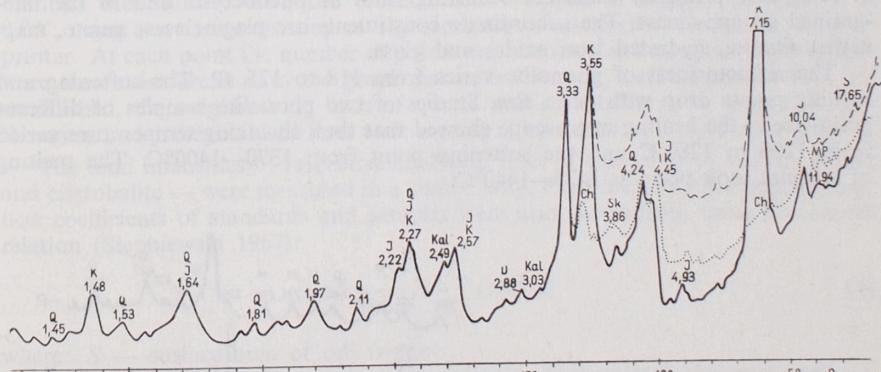


Fig. 1. X-ray diffraction patterns of clay from Łęknica

a —— sedimented sample, b —— glycerated sample, c . . . sample heated at 600°C; K — kaolinite, I — illite, S — smectite, MP — mixed-layer minerals, Ch — chlorite, Q — quartz, Kal — calcite, D — dolomite

content of mullite, cristobalite, quartz and other crystalline constituents, as well as that of glass phase, is of prime importance. The phase composition and the texture of clays in the burnt state determine the properties of ceramic ware, such as apparent density, water absorption and compressive strength.

The present authors made an attempt to modify the phase composition, and therefore the properties, of clays in the burnt state by an addition of substances that are active at high temperatures and enter into reactions with the mineral components of clays. In the unburnt state they have a tempering effect, the same as quartz, diminishing the plasticity and shrinkage of clays. Fly-ash from the Turów power plant in Turoszów and powdered trachytic phonolite from Opolno Zdrój were used as modifying agents.

Fly-ash from Turoszów consists mainly of mullite and glass phase. Its phase and chemical compositions are close to those of burnt kaolinite clays. Fly-ash has been used to-date as a component of stoneware mixes and engineering bricks and has been found to promote the crystallization of mullite in these materials (Paciak 1977, Ropska 1980, Tokarski 1969). It has, however, a very high melting point, and its introduction in greater amounts as a batch component increases markedly the water absorption (wt.%) and decreases the compressive strength of ware (Antonowicz 1973). Fly-ash is a fine-grained substance in which grains < 60 μm prevail.

Phonolite from Opolno Zdrój is a rock with low melting point (1370—1400°C). Its melt has low viscosity due to the high sodium content. Owing to this property, it is used as a batch component for the manufacture of stoneware because it decreases water absorption (Lewowicki 1978 a). The stoneware acquires optimum properties when phonolite is added together with fly-ash because then its strength increases (Lewowicki 1978 b, 1979 a, b).

The aim of this paper was to investigate the effect of fly-ash and phonolite on the properties of burnt clays and to find regularities controlling the changes in their phase composition.

EXPERIMENTAL

Materials

Investigations were carried out on grey plastic clay of a refractoriness of 165 sP from the "Irena" mine at Łęknica. The amount of < 20 μm fractions in the grain-size composition of the sample totalled 70%, 26% falling to the < 0.5 μm fraction. The chemical analysis of the untreated sample and the separated < 0.5 μm fraction is presented in Table 1. As is evident from the analysis, the principal component of the clay is clay minerals of the kaolinite series, with illite appearing as a subordinate constituent. The intensities of basal kaolinite and illite lines in X-ray diffraction patterns (Fig. 1) confirm the predominance of kaolinite. Lines noted in the low-angle range testify to the presence of trace amounts of smectite and mixed-layer minerals. Non-clay minerals are represented by quartz and small amounts of feldspars, calcite and dolomite. The diffraction pattern of a sample heated at 600°C also points to the presence of trace chlorite.

The above quantitative ratios of clay minerals, both in the untreated sample and in its finest fraction, have been confirmed by thermal analysis (Fig. 2). The DTA curve with its two peaks, endothermic at 560°C and exothermic at 930°C, points to the dominant content of kaolinite in the clay.

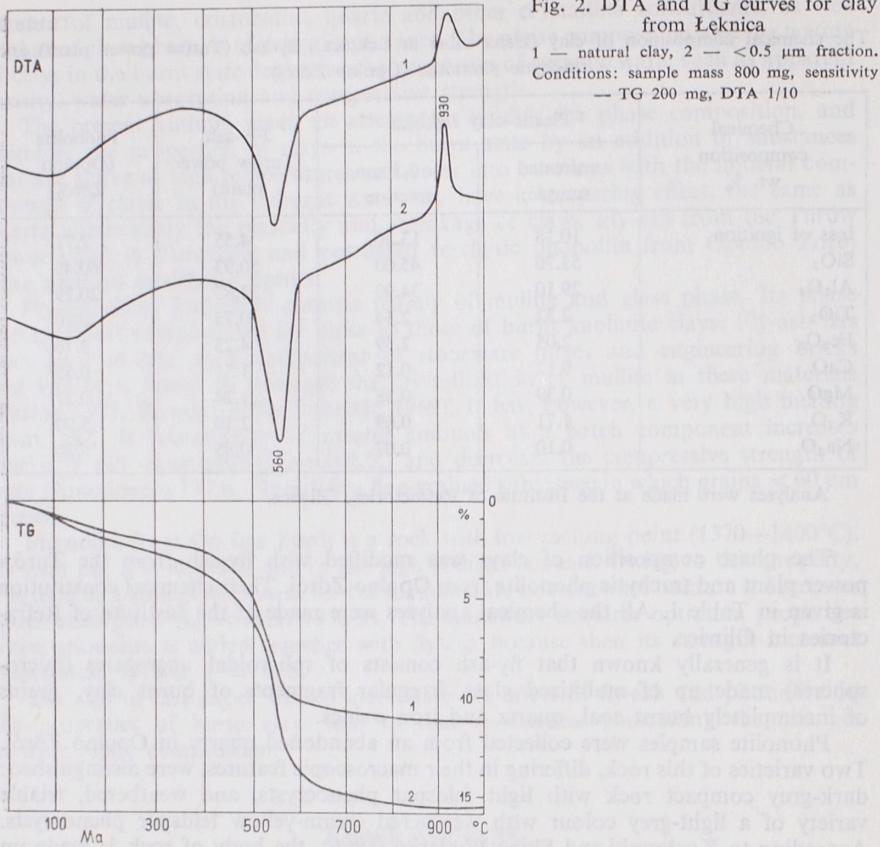


Fig. 2. DTA and TG curves for clay from Łęknica

1 — natural clay, 2 — $<0.5 \mu\text{m}$ fraction.
Conditions: sample mass 800 mg, sensitivity — TG 200 mg, DTA 1/10

of feldspars, primarily sanidine, occurring both as phenocrysts and in the fine-grained ground-mass. The subordinate constituents are plagioclases, augite, magnetite, hydrated iron oxides and glass.

The refractoriness of phonolite varies from 118 to 125 sP. The softening and melting points drop with grain size. Studies of two phonolite samples of different grain-size in the heating microscope showed that their shrinking temperature varied from 1250 to 1280°C and the softening point from 1370—1400°C. The melting of samples took place at 1425—1440°C.

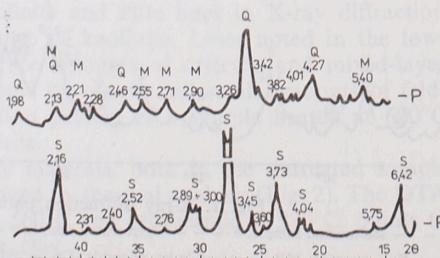


Fig. 3. X-ray diffraction patterns of phonolite and fly-ash from Turów power plant

F — phonolite, P — fly-ash, S — feldspars, Q — quartz, M — mullite

The phase composition of fly-ash and phonolite is shown in Figure 3. Feldspars predominate in the phonolite sample, their strongest lines appearing in the range of 27—28° 2θ. The X-ray diffraction pattern of ash revealed mainly mullite and quartz among its crystalline components.

Methods

It was assumed that the most expedient step in determining the effect of fly-ash and phonolite and the properties of burnt clay from Łęknica was to establish the phase composition of samples fired at 1180, 1240 and 1300°C. Such temperatures were chosen with the object of following the phase changes occurring over a wide range of clay burning temperatures.

The second aim of the studies was to determine the immediate effect of the non-clay additives on the physico-mechanical properties of burnt clays, i.e. on their apparent density, water absorption (wt.%) and compressive strength.

The resulting data on the phase composition were compared with the mechanical properties of burnt bodies, and the relations between them were established using the method of regression analysis.

The experimental procedure was as follows: The clay was dried at 110°C, broken up in a crusher, and pre-set amounts of ash and phonolite of grain-size less than 0.5 mm were added. When the batch constituents were plasticized with make-up water, plates with the dimensions of 80 × 40 × 25 mm and cubes of 60 × 60 × 60 mm were formed in a hand press. After drying at 110°C, the plates and cubes were fired in an electric furnace at pre-set temperatures. The samples were placed in a muffle to minimize the temperature variations inside the furnace chamber.

The samples prepared in this way were subjected to qualitative and quantitative X-ray analysis and their apparent density, water absorption and compressive strength were measured. Apparent density and water absorption were determined on plates, while compressive strength and phase composition on cubes.

The phase composition of burnt clays was determined by means of internal standard (Zewin, Zawiłowa 1974). On the basis of preliminary qualitative analysis, the following lines were chosen: mullite — 0.540 nm, quartz — 0.427 nm, cristobalite — 0.408 nm (5.40, 4.27, 4.08 Å). The angle range of 7.5—12° 2θ (CuK_α radiation) was scanned with the diffractometer stepped in angular increments of 0.04°, using a system consisting of a goniometer — analyser — electronic scaler — printer. At each point the number of pulses was counted for 1 minute. The printouts were then transferred onto the graph paper, whereupon the background line was established, the neighbouring lines of quartz and cristobalite were separated, and the areas under the analysed lines were measured by means of a planimeter (Fig. 4).

The total intensities of respective analytical lines of standards — mullite, quartz and cristobalite — were measured in a similar way. Experimentally the mass absorption coefficients of standards and samples were also determined, using the known relation (Stępniewski 1967):

$$\mu^x = \frac{S}{m} \ln \frac{I_o}{I_i} (\text{cm}^2/\text{g}) \quad (1)$$

where: S — surface area of cell window,

I_o — intensity of monochromatic beam passing through the empty cell,

I_i — intensity of monochromatic beam passing through the cell containing a sample,

m — mass of the pressed sample.

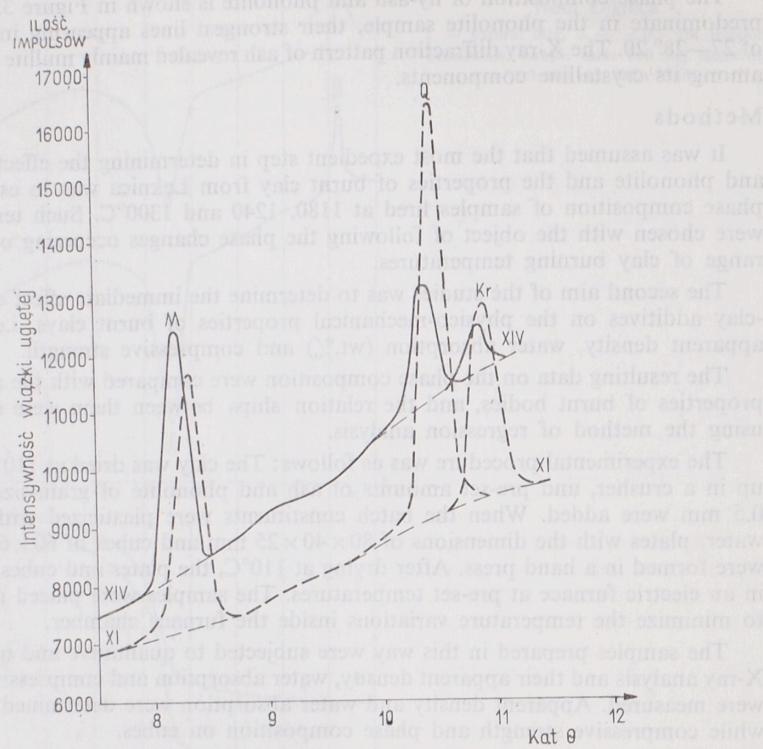


Fig. 4. X-ray diffraction patterns serving as a basis for quantitative phase analysis of ceramic ware
XI—XI, XII—XIV—numbers of batches according to computer programme; M—mullite, Kr—cristobalite, Q—quartz

The percentage composition was calculated from the formula given by Klug and Alexander (1954):

$$X_{ij} = \frac{I_{ij}^m \cdot \mu_j^x}{I_{io}^m \cdot \mu_{io}^x} \cdot 100 \% \quad (2)$$

where: I_{ij}^m — intensity of the analytical line of i-th phase of j-th sample,
 I_{io}^m — intensity of the analytical line of the i-th phase standard,
 μ_j^x — mass absorption coefficient of j-th sample,
 μ_{io}^x — mass absorption coefficient of the i-th phase standard,
 x_{ij} — content of i-th phase in j-th sample.

For lack of standards, the content of glass phase in samples was only estimated from the raised background testifying to the presence of this phase. The band in the range 0.35–0.45 nm was analysed (Stoch, Świątek 1977), and the measurements of the band height above the background are shown in Fig. 5 (the results are given in mm). To determine approximately the percentage values corresponding to these data, a similar measurement was made on a glass sample obtained upon melting of phonolite. The maximum band height above the background was in this case 60 mm, which corresponds approximately to 100% of the phase, without taking into account the mass absorption coefficient of glass. Relatively, every 10 mm may be

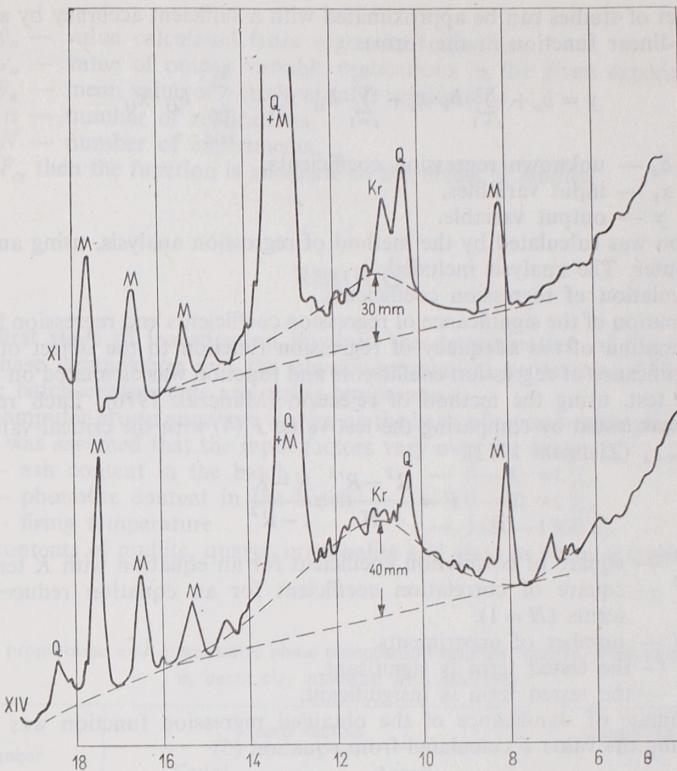


Fig. 5. X-ray diffraction patterns serving as a basis for the determination of glass content in burnt clay samples
Q — quartz, M — mullite, Kr — cristobalite

regarded as approximately corresponding to the formation of 15% of glass in burnt samples.

X-ray analysis of phase composition was carried out with a TUR M-61 diffractometer, using filtered CuK_α radiation. The instrument settings were: voltage 30 kV, tube current 25 mA, scanning speed $1^\circ/\text{min.}$, chart speed 1200 mm/hr, number of counts $18 \cdot 10^3$, slits: at the tube 2 and 1 mm, at the detector 2 mm.

The physical properties of clays after burning, viz. total shrinkage, water absorption and apparent density, were determined on plates whereas compressive strength was tested on cubes. Each result given in this paper is the mean of three measurements.

MATHEMATICAL DESIGN OF EXPERIMENTS

The technique of design of experiments was adopted to achieve the aim set out in this paper (Gorockiewicz et al. 1982, Mańczak 1976, Polański 1978). Basing on the available data it was assumed that the unknown mathematical characteristic

of the object of studies can be approximated with a sufficient accuracy by a second-order non-linear function in the form:

$$y = b_o + \sum_{s=1}^S b_s \cdot x_s + \sum_{s=1}^{S_s} b_{ss} \cdot x_{ss}^2 + \sum_{\substack{i,j=1 \\ i < j}}^{S_s} b_{ij} \cdot x_{ij} \quad (3)$$

where: b_o, b_s — unknown regression coefficients,
 x_s — input variables,
 y — output variable.

The function was calculated by the method of regression analysis, using an ODRÁ 1304 computer. The analysis included:

- the calculation of regression coefficients,
- the estimation of the significance of regression coefficients and regression function,
- the estimation of the adequacy of regression function to the object of studies.

The significance of regression coefficients and function was estimated on the basis of Fisher's test, using the method of rejection (Mańczak 1976). Each regression coefficient was tested by comparing the test value F (4) with the critical value $F_{cr} = F_{0.05; 1; N-K}$ (Zielinski 1972).

$$F = \frac{R^2 - R'^2}{H} \cdot \frac{N-K}{1-R^2} \quad (4)$$

where: R^2 — square of correlation coefficient for an equation with K terms,
 R'^2 — square of correlation coefficient for an equation reduced by H terms ($H=1$),
 N — number of experiments.

If: $F \geq F_{cr}$ — the tested term is significant,
 $F < F_{cr}$ — the tested term is insignificant.

The estimate of significance of the obtained regression function was checked by comparing the value F calculated from equation (5)

$$F = \frac{R^2}{K-1} \cdot \frac{N-K}{1-R^2} \quad (5)$$

where: R^2 — square of correlation coefficient for an equation with significant terms,

K — number of regression coefficients in an equation (number of terms),
 N — number of experiments,

with the critical value $F_{0.05; K-1; N-K}$.

If $F \geq F_{cr}$ then the function is significant; if $F < F_{cr}$ — the function is insignificant.

The adequacy of the regression function to the object of studies was estimated by comparing the value F_{ad} calculated from relation (6) with the critical value $F_{0.05; N-K; n-1}$.

$$F_{ad} = \frac{S_R^2}{S_e^2}; \quad S_R^2 = \frac{S_R}{N-K-n-1}; \quad S_e^2 = \frac{S_e}{n-1} \quad (6)$$

where: S_R^2 — residual variance — $S_R = \sum_{u=1}^N (\bar{y}_u - \hat{y}_u)^2$,

S_e^2 — measuring error variance — $S_e = \sum_{a=1}^n (y_a - \bar{y}_a)^2$,

\bar{y}_u — mean value of output variable obtained at a given measuring point (experimental),

\hat{y}_u — value calculated from regression equation,

y_a — value of output variable replications in the given experiment,

\bar{y}_a — mean value of output variable replications,

n — number of replications,

N — number of experiments.

If $F_{ad} \leq F_{cr}$ then the function is adequate to the object of studies.

RESULTS

The first stage of investigation involved the determination of the dependence of the phase composition and the physico-mechanical properties of burnt bodies upon the batch components and firing temperature.

The computer programme was written on the basis of second-order plan (Mańczak 1976). It was assumed that the input factors vary over the range:

X_1 — ash content in the batch	— 0–30 wt.%,
X_2 — phonolite content in the batch	— 0–40 wt.%,
X_3 — firing temperature	— 1180–1300°C.

The contents of mullite, quartz, cristobalite and glass in burnt samples are given

Table 2
Computer programme and quantitative phase composition (mullite, quartz, cristobalite and glass) in burnt clay modified with additives

Number of experiment	Input factors						Output factors			
	Coded			Actual			M %	Q %	K %	Sz mm
	X_1	X_2	X_3	$X_1, \%$	$X_2, \%$	$X_3, ^\circ C$				
1	—	—	—	0	0	1180	21	24	7	22
2	—	+	—	0	40	1180	10	8	2	36
3	—	—	+	0	0	1300	31	15	10	30
4	+	—	—	30	0	1180	26	18	2	20
5	+	+	—	30	40	1180	17	12	3	33
6	—	+	+	0	40	1300	17	23	1	37
7	+	—	+	30	0	1300	27	12	3	29
8	+	+	+	30	40	1300	17	6	1	30
9	—	0	0	0	20	1240	20	15	1	37
10	+	0	0	30	20	1240	24	11	1	27
11	0	—	0	15	0	1240	31	22	5	30
12	0	+	0	15	40	1240	17	8	0	31
13	0	0	—	15	20	1180	18	13	1	30
14	0	0	+	15	20	1300	24	7	1	40
15	0	0	0	15	20	1240	19	11	1*)	35
16	0	0	0	15	20	1240	19	15	1*)	37
17	0	0	0	15	20	1240	18	10	1*)	36
18	0	0	0	15	20	1240	22	13	1*)	34
19	0	0	0	15	20	1240	23	10	1*)	37

*) Value rounded up to a whole number.

Table 3
Regression analysis of the dependence of mullite, quartz, cristobalite and glass content on the components added to clays and on firing temperature

Number of regression coefficient	Mullite	Quartz	Cristobalite	Glass
	Significant regression coefficients			
b_0	21.44	11.74	0.814	35.27
b_1	2.1	-2.6	-1.1	-2.3
b_2	-6.7	-3.4	-2.0	3.6
b_3	3.3	-1.2	—	2.5
b_{12}	1.875	—	1.625	—
b_{13}	-3.125	-2.25	-0.375	-0.875
b_{23}	—	-3.0	-0.875	-2.375
b_{11}	—	1.33	0.417	-2.204
b_{22}	—	3.33	1.917	-3.704
b_{33}	-1.544	-1.67	0.417	—
Square of correlation coefficient R^2	0.931	0.732	0.961	0.850
Estimate of regression equation	$F = 26.76 > F_{0.05-6-12} = 3.00$ significant	$F = 3.41 > F_{0.05-8-10} = 3.07$ significant	$F = 30.8 > F_{0.05-8-10} = 3.07$ significant	$F = 8.3 > F_{0.05-8-11} = 3.01$ significant
Residual variance S_e^2	6.62	19.24	0.74	9.68
Measuring error variance S_e^2	4.7	4.1	0*)	1.7
Estimate of regression function adequacy	$F_{ad} = 1.41 < F_{0.05-8-4} = 6.04$ adequate	$F_{ad} = 4.09 < F_{0.05-6-4} = 6.16$ adequate		$F_{ad} = 5.7 < F_{0.05-7-4} = 6.09$ adequate

*) The value is a result of the limited sensitivity of measuring method.

in Table 2. From measurements and calculations (Table 3) the following regression equations were obtained:

$$M = 21.44 + 2.1 \frac{X_p - 15}{15} - 6.7 \frac{X_F - 20}{20} + 3.3 \frac{T_w - 1240}{60} + 1.875 \frac{X_p - 15}{15} \cdot \frac{X_F - 20}{20} + \\ - 3.125 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} - 1.544 \left(\frac{T_w - 1240}{60} \right)^2 \quad (7)$$

$$Q = 11.74 - 2.6 \frac{X_p - 15}{15} - 3.4 \frac{X_F - 20}{20} - 1.2 \frac{T_w - 1240}{60} - 2.25 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} + \\ - 3.0 \frac{X_F - 20}{20} \cdot \frac{T_w - 1240}{60} + 1.33 \left(\frac{X_p - 15}{15} \right)^2 + 3.33 \left(\frac{X_F - 20}{20} \right)^2 - 1.67 \left(\frac{T_w - 1240}{60} \right)^2 \quad (8)$$

$$K = 0.814 - 1.1 \frac{X_p - 15}{15} - 2.0 \frac{X_F - 20}{20} + 1.625 \frac{X_p - 15}{15} \cdot \frac{X_F - 20}{20} + \\ - 0.375 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} - 0.875 \frac{X_F - 20}{20} \cdot \frac{T_w - 1240}{60} + 0.417 \left(\frac{X_p - 15}{15} \right)^2 + \\ + 1.917 \left(\frac{X_F - 20}{20} \right)^2 + 0.417 \left(\frac{T_w - 1240}{60} \right)^2 \quad (9)$$

$$Sz = 35.27 - 2.3 \frac{X_p - 15}{15} + 3.6 \frac{X_F - 20}{20} + 2.5 \frac{T_w - 1240}{60} - 0.875 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} + \\ - 2.375 \frac{X_F - 20}{20} \cdot \frac{T_w - 1240}{60} - 2.204 \left(\frac{X_p - 15}{15} \right)^2 - 3.704 \left(\frac{X_F - 20}{20} \right)^2 \quad (10)$$

where: M — mullite content, vol.%;
 Q — quartz content, vol.%;
 K — cristobalite content, vol.%;
 Sz — estimate of glass content (raised background in mm);
 X_p — ash content, wt.%;
 X_F — phonolite content, wt.%;
 T_w — firing temperature, °C.
 Some examples of graphical interpretation of the regression equations are shown in Figures 6—11.

From regression equation (7) and figures 6, 7 it appears that mullite content in clays increases with firing temperature, the presence of phonolite in the mix affecting adversely the formation of this phase. At low firing temperatures the amount of mullite increases with the increasing ash content. With the rise in temperature, from about 1240°C, mullite content decreases with the increasing ash addition, especially when phonolite content is low.

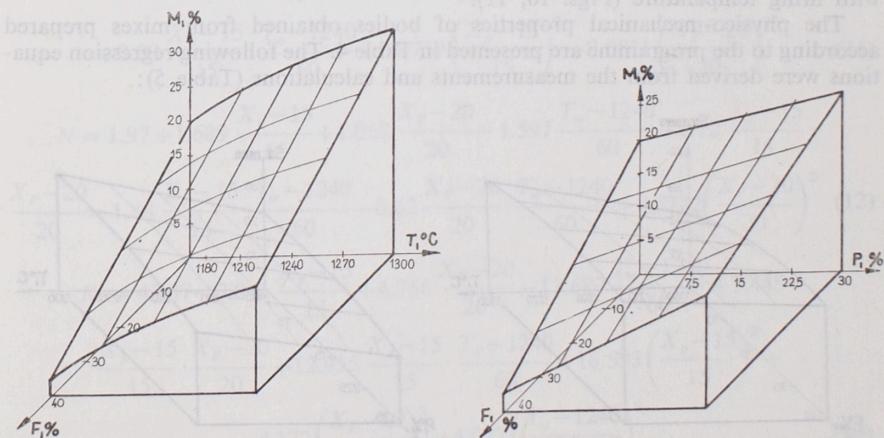


Fig. 6. Plot of mullite (M) content vs. fly-ash (F) content in the batch and firing temperature (T)

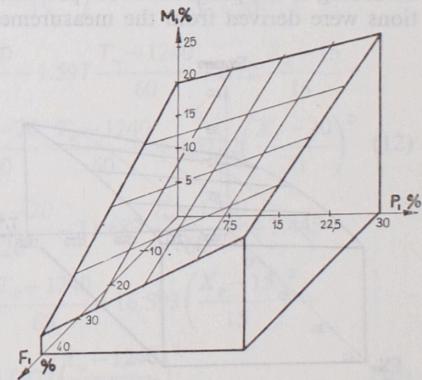


Fig. 7. Plot of mullite (M) content vs. fly-ash (P) and phonolite (F) content in the batch after burning at 1180°C

Table 4

Computer programme and apparent density, water absorption and compressive strength of modified clays after burning

Number of experiment	Input factors			Output factors*)					
	Coded			Actual					
	X_1	X_2	X_3	$X_1, \%$	$X_2, \%$	$X_3, ^\circ\text{C}$			
1	—	—	—	0	0	1180	2.34	63.9	0.75
2	—	+	—	0	40	1180	2.09	84.0	1.10
3	—	—	+	0	0	1300	2.08	37.2	0.55
4	+	—	—	30	0	1180	1.96	51.3	4.55
5	+	+	—	30	40	1180	2.01	46.3	10.04
6	—	+	+	0	40	1300	1.79	17.7	0.68
7	+	—	+	30	0	1300	1.95	37.5	0.69
8	+	+	+	30	40	1300	2.10	70.7	1.44
9	—	0	0	0	20	1240	2.25	79.4	0.79
10	+	0	0	30	20	1240	2.00	45.9	4.04
11	0	—	0	15	0	1240	2.03	32.5	0.85
12	0	+	0	15	40	1240	2.04	51.9	4.75
13	0	0	—	15	20	1180	2.05	59.3	3.58
14	0	0	+	15	20	1300	1.89	24.8	0.69
15	0	0	0	15	20	1240	2.08	41.4	1.98
16	0	0	0	15	20	1240	2.02	35.0	1.53
17	0	0	0	15	20	1240	2.03	39.9	1.95
18	0	0	0	15	20	1240	2.06	35.1	1.70
19	0	0	0	15	20	1240	2.07	54.6	1.45

*) Mean of three measurements.

$$G = 2.048 - 0.053 \frac{X_p - 15}{15} - 0.064 \frac{T_w - 1240}{60} + 0.0925 \frac{X_p - 15}{15} \cdot \frac{X_F - 20}{20} + 0.08 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} + 0.0739 \left(\frac{X_p - 15}{15} \right)^2 - 0.0811 \left(\frac{X_F - 20}{20} \right)^2 \quad (11)$$

$$N = 1.97 + 1.689 \frac{X_p - 15}{15} + 1.062 \frac{X_F - 20}{20} - 1.597 \frac{T_w - 1240}{60} + 0.72 \frac{X_p - 15}{15} \cdot \frac{X_F - 20}{20} - 1.48 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} - 0.62 \frac{X_F - 20}{20} \cdot \frac{T_w - 1240}{60} + 0.5722 \left(\frac{X_F - 20}{20} \right)^2 \quad (12)$$

$$R_c = 43.37 - 3.041 \frac{X_p - 15}{15} + 4.756 \frac{X_F - 20}{20} - 11.689 \frac{T_w - 1240}{60} + 3.445 \cdot \frac{X_p - 15}{15} \cdot \frac{X_F - 20}{20} + 12.955 \frac{X_p - 15}{15} \cdot \frac{T_w - 1240}{60} + 16.593 \left(\frac{X_p - 15}{15} \right)^2 - 4.172 \left(\frac{X_F - 20}{20} \right)^2 - 4.027 \left(\frac{T_w - 1240}{60} \right)^2 \quad (13)$$

where: G — apparent density, Mg/m^3 ,
 N — water absorption, wt.%,

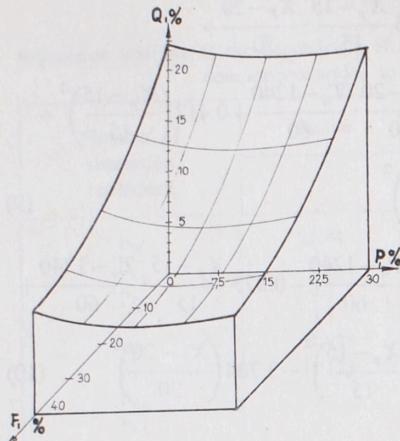


Fig. 8. Plot of quartz (Q) content vs. fly-ash (P) and phonolite (F) content in the batch after burning at 1180°C

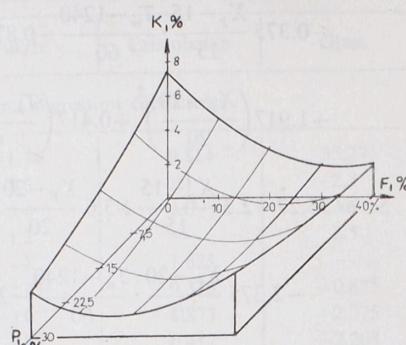


Fig. 9. Plot of cristobalite (K) content vs. fly-ash (P) and phonolite (F) content in the batch after burning at 1180°C

Equation (8) and Figure 8 show that quartz content decreases with the increasing firing temperature and phonolite content. The addition of fly-ash does not virtually affect the amount of quartz in clays burnt at low temperatures, while at higher temperatures the increase in ash addition results in the decrease in quartz content.

According to equation (9), cristobalite content in clays increases with rising temperature. The addition of phonolite diminishes the amount of cristobalite in the ware (Fig. 9).

As appears from equation (10), changes in glass content as a function of temperature and the amount of ash and phonolite in the mix are similar to the variation of mullite content vs. these parameters. In general, glass content in clays increases with firing temperature (Figs. 10, 11).

The physico-mechanical properties of bodies obtained from mixes prepared according to the programme are presented in Table 4. The following regression equations were derived from the measurements and calculations (Table 5):

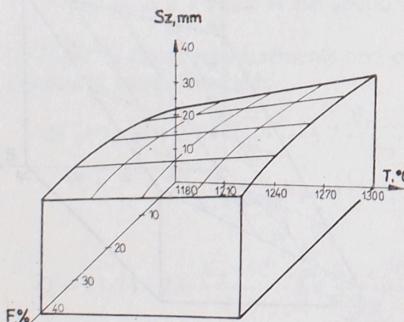


Fig. 10. Plot of glass (Sz) content vs. phonolite (F) content in the batch and firing temperature (T)

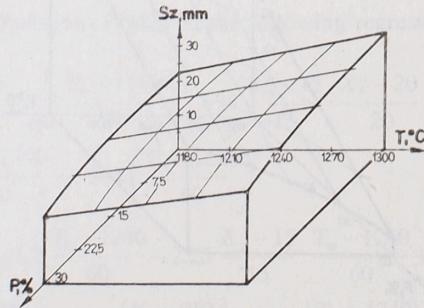


Fig. 11. Plot of glass (Sz) content vs. fly-ash (P) content in the batch and firing temperature (T)

Table 5

Regression analysis of the dependence of apparent density, water absorption and compressive strength of clays on modifying additives and firing temperature

Number of regression coefficient	Significant regression coefficients		
	Apparent density	Compressive strength	Porosity
b_0	2.048	43.37	1.97
b_1	-0.053	-3.041	1.689
b_2	—	4.756	1.062
b_3	-0.064	-11.689	-1.598
b_{12}	0.0925	3.445	0.72
b_{13}	0.08	12.955	-1.48
b_{23}	—	—	-0.62
b_{11}	0.0739	16.593	—
b_{22}	-0.0811	-4.172	0.5722
b_{33}	—	-4.027	—
Square correlation coefficient R^2	0.862	0.77	0.941
Estimate of regression equation significance	$F = 9.47$ $F_{0.05-6-12} = 3.00$ significant	$F = 4.18$ $F_{0.05-8-10} = 3.07$ significant	$F = 25.02$ $F_{0.05-7-11} = 3.01$ significant
Residual variance	0.00426	281.35	0.82
Measuring error variance S_e^2	0.161	64.13	13.31
Estimate of regression function adequacy	$F_{ad} = 0.027$ $F_{0.05-8-4} = 6.04$ adequate	$F_{ad} = 4.39$ $F_{0.05-6-4} = 6.16$ adequate	$F_{ad} = 0.07$ $F_{0.05-7-4} = 6.09$ adequate

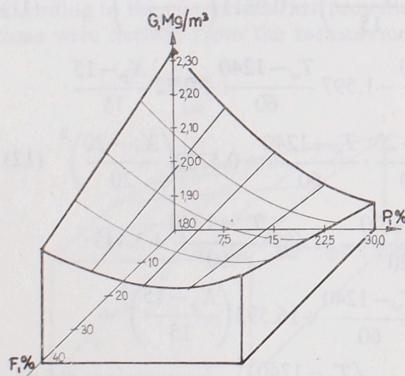


Fig. 12. Plot of apparent density (G) of clay samples fired at 1180°C vs. the amount of additives: fly-ash (P) and phonolite (F)

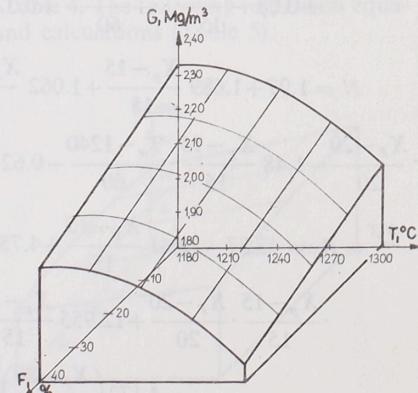


Fig. 13. Plot of apparent density (G) of clay samples modified with phonolite (F) vs. firing temperature (T)

R_c — compressive strength, MPa,
 X_p — ash content, wt.%,
 X_F — phonolite content, wt.%,
 T_w — firing temperature, °C.

The graphical interpretation of the regression equations is shown in figures 12–18.

From regression equation (11) and Figures 12, 13 it is evident that unmodified clays fired at 1180°C have the highest apparent density. In general, apparent density diminishes as firing temperature is raised. It can also be stated that ash or phonolite added to clay decreases the density of ware.

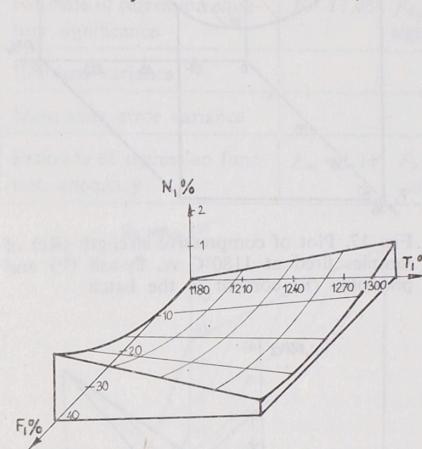


Fig. 14. Plot of water absorption (N) vs. phonolite (F) content in the batch and firing temperature (T)

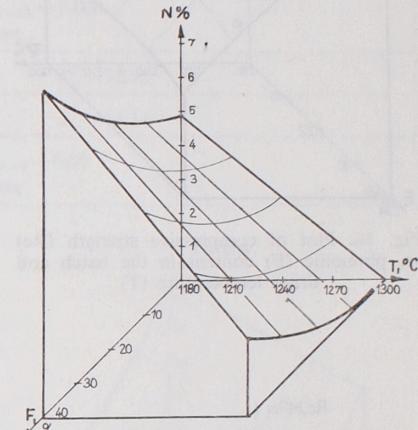


Fig. 15. Plot of water absorption (N) vs. firing temperature (T) in samples having a constant fly-ash content (30%) and variable phonolite (F) content

On the basis of equation (12) and Figures 14, 15 it has been found that there is only a weak correlation between the water absorption of burnt samples, temperature and phonolite addition if ash content is very low (cf. Fig. 14). When the addition of ash is substantial (Fig. 15), the dependence of water absorption upon firing temperature becomes significant, the higher the temperature, the lower the water absorption. Phonolite addition also affects to a certain extent the water absorption of the ware, this being the greater, the higher is the ash content.

The highest compressive strength (equation 13) is obtained in the ware burnt from pure clay or from clay with phonolite (Fig. 16). An increase in ash content in the mix causes a rapid deterioration in the strength of samples fired at low temperatures (Fig. 17), irrespective of the amount of phonolite added. At the same time the strength of samples fired at about 1240°C increases when the content of ash in the mix is more than 15 wt.%. Further increase in strength is effected by adding more phonolite to the clay (Fig. 18).

Further investigations of the effect of the phase composition and apparent density of materials on their strength are presented in Table 6. The following regression equation was derived:

$$R_c = 201.57 - 1.587 \cdot M - 13.86 \cdot S_z + 3.698 S_z \cdot G + 0.2535 Q \cdot G + 0.0855 S_z^2 \quad (14)$$

where: R_c — compressive strength, MPa,
 M — mullite content, vol.%,

Table 6

Regression analysis of the dependence of compressive strength on the phase composition and apparent density of modified clays

Significant regression coefficients	b_0	b_1	b_2	b_{24}	b_{34}	b_{22}
	201.57	-1.587	-13.86	3.698	0.2535	0.0855
Square of correlation coefficient	$R^2 = 0.895$					
Estimate of regression equation significance	$F = 17.05 \quad F_{0.05-6-12} = 3.000$ significant					
Residual variance	$S_R^2 = 72.92$					
Measuring error variance	$S_e^2 = 64.14$					
Estimate of regression function adequacy	$F_{ad} = 1.14 \quad F_{0.05-9-4} = 6.00$ adequate					

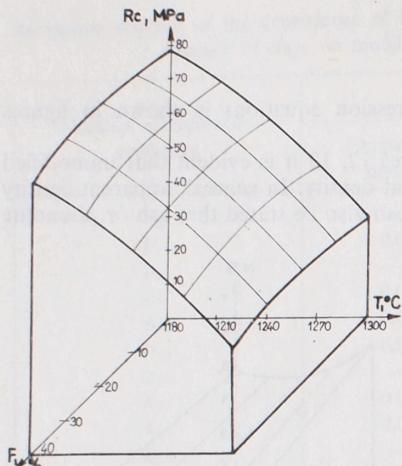


Fig. 16. Plot of compressive strength (Rc) vs. phonolite (F) content in the batch and firing temperature (T)

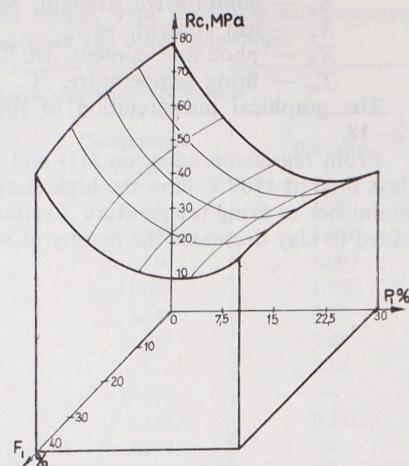


Fig. 17. Plot of compressive strength (Rc) of samples fired at 1180°C vs. fly-ash (P) and phonolite (F) content in the batch

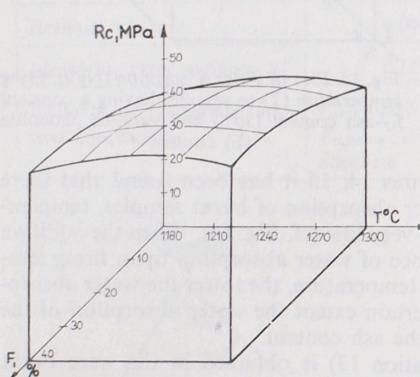


Fig. 18. Plot of compressive strength (Rc) vs. firing temperature (T) in samples having a constant ash content (30%) and variable phonolite (F) content

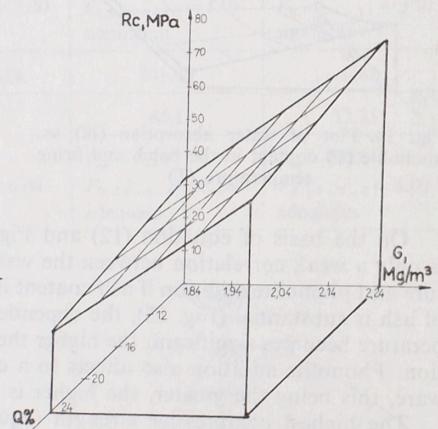


Fig. 19. Plot of compressive strength (Rc) vs. apparent density (G) and quartz (Q) content at the constant content of mullite (20%) and glass (about 45%) in the ware

Q — quartz content, vol.%;
 Sz — estimate of glass content, mm,
 G — apparent density, Mg/m^3 .

From equation (14) and Figures 19—21 it may be inferred that when the density of samples is low, the increase in the percentage of glass and mullite is attended by the decrease in strength, irrespective of quartz content. It has also been found that the increased glass content affects the strength of ware in a less degree than the high

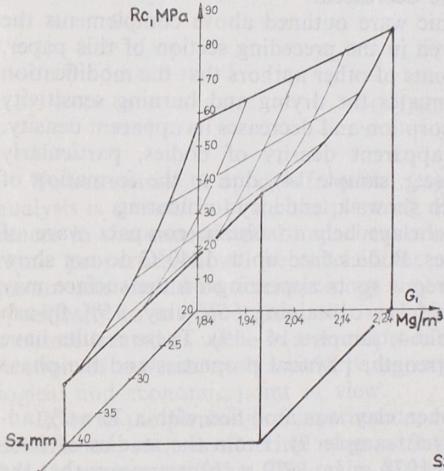


Fig. 20. Plot of compressive strength (Rc) vs. apparent density (G) and glass (Sz) content at the constant content of mullite (20%) and quartz (12%) in the ware

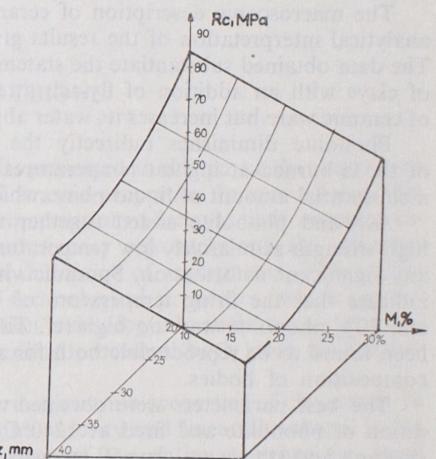


Fig. 21. Plot of compressive strength (Rc) vs. mullite and glass content in the ware at a constant apparent density of $2.04 \text{ Mg}/\text{m}^3$ and a quartz content of 16%

mullite content (Fig. 21). The ware shows high compressive strength also in the case when it contains a large amount of glass phase but has high density as well (cf. Fig. 20).

DISCUSSION

Studies were carried out on stoneware obtained from batches consisting of clay, fly-ash and phonolite mixed in various proportions. Two out of the nineteen batches were composed of pure clay. Their total shrinkage was 14.6% at an apparent density of $2.34 \text{ Mg}/\text{m}^3$. Fired at 1180 and 1300°C, the samples in question (1 and 3) showed

deformation due to excessive linear shrinkage. Burning at the maximum temperature (1300°C) produced vitreous spots on the surface and inside the ware, as well as cracks parallel to the basal planes. The strength of sample 3 was diminished nearly by a half compared with the strength of sample 1 fired at a lower temperature (1180°C).

Though the modification of clay with fly-ash (samples 4, 7, 11) brought about a decrease in shrinkage, it did not prevent the deformation or microcracking of the ware.

The modification of clay with a phonolite addition (samples 2, 6, 9) and its burning up to 1240°C eliminated deformation, made the ware compact and increased its mechanical strength (samples 2, 9). However, burning at higher temperatures produced a microporous structure, deformations, vitreous spots and surface roughness in the ware. Moreover, the compressive strength of the ware deteriorated rapidly (sample 6).

Bodies obtained from clays with additions of ash and phonolite (samples 8, 10, 12–19) and fired at temperatures up to 1240°C did not exhibit any deformation, cracking or vitreous spots. Yet they showed a tendency to form a microporous structure. At 1300°C (sample 14) a porous, locally bloated body formed, with the surface made rough by numerous vitreous spots. Simultaneously the compressive strength and apparent density of the ware decreased.

The macroscopic description of ceramic ware outlined above complements the analytical interpretation of the results given in the preceding section of this paper. The data obtained substantiate the statements of other authors that the modification of clays with an addition of fly-ash attenuates the drying and burning sensitivity of ceramic ware but increases its water absorption and decreases its apparent density.

Phonolite diminishes indirectly the apparent density of bodies, particularly of those burned at highest temperatures (e.g. sample 14), due to the formation of a substantial amount of liquid phase which shows a tendency to bloating.

Ash and phonolite added together to clays help to obtain compact ware of high strength at relatively low temperatures. Bodies fired up to 1240°C do not show any significant deformation. Sporadic vitreous spots appearing on the surface may indicate that the firing temperature of batches containing 65% clay, 15% fly-ash and 20% phonolite was too high (cf. Table 4, samples 14–19). These results have been found to be reproducible both for strength, physical properties and the phase composition of bodies.

The best parameters were obtained when clay was modified with a 20 wt.% addition of phonolite and fired at 1240°C (cf. sample 9). From the studies of low-melting and stoneware clays (Lewowicki 1978 a, b, 1979 a, b) it appears that the best strength and water absorption characteristics are obtained when clays are modified with ash and phonolite in the proportion: 50% clay, 30% ash and 20% phonolite. The rise in burning temperature is attended by the increase in glass phase content and by a change in quantitative ratios of crystalline phases.

From the regression equation (14) it follows that with an increase in glass and mullite content and the simultaneous decrease in apparent density, the strength of ware deteriorates, while an increase in glass content accompanied by the increase in apparent density ensures the high strength of the ware.

The studies of other authors have shown that the effect of mullite on the strength of ceramic ware is as follows: Secondary mullite crystallizes from the melt and enhances the mechanical properties of glass only if long (150–1000 µm), filamentous crystals are formed to give a compact fibrous texture. This can be accomplished by using mineralizers (NaF, LiF) and appropriately programmed cooling schedules for the ware after burning (Groszewska et al. 1971). In the ware obtained from modified clays from Łeknica, it is needle-like secondary mullite of a crystal length up to

25 µm that fills up isolated oval or less commonly, elongate pores or cracks in the microporous glass matrix of the body. Such a structure was observed with a scanning microscope in HF-treated samples.

Mullite ceramics owe their high strength to the presence of fibrous crystals making up more than 70% of the body, cemented with glass phase. When the amount of mullite monocrystals is small, a secondary crystalline phase, e.g. α -cristobalite, crystallizes from the glass matrix, deteriorating the mechanical strength of the ware. The mechanical testing of mullite ware has shown that the weakest points in the structure are the boundaries between glass and mullite. In polycrystalline ceramic ware weak points are also the boundaries between phases with different coefficients of thermal expansion, which generates stresses at the grain boundaries (Groszewska et al. 1971).

The studies of the process of crystallization that takes place during the heating of aluminosilicate fibres with a composition of kaolinite (Gaodu et al. 1977) have shown that the principal phase is mullite which crystallizes intensely over a temperature range 1100–1200°C. This process is responsible for the deterioration in strength and the increase in shrinkage, these being the greater the higher was the degree of crystallization.

CONCLUSIONS

To summarize, it appears from the results presented in this paper that regression analysis is a useful tool for the planning of ceramic properties. In view of the differences in the mineralogical and chemical compositions of clays, their essential ceramic properties should be checked for each variety separately and the optimum parameters should be determined by way of the design of experiments. This applies specifically to raw materials with variable technological properties, which are sometimes treated as waste in a given production technology. In such cases, the modification of raw materials would be an expedient procedure both from the technological and economic point of view.

Prior to the planning of experiments, certain ceramic properties of clays must be determined, such as sintering range, strength, porosity and linear shrinkage. It has been demonstrated that the main determinant of the optimum properties (high strength, low shrinkage and water absorption) of ware obtained from Łeknica clays is their modification with phonolite added in an amount of 20–40 wt.%. The resulting ware with a strength of more than 70 MPa, water absorption of about 1 wt.% and a total shrinkage of about 12% meets the specifications for acid-proof stoneware of KW-1 grade, as well as those for special chemical stoneware of grade I (KS).

Bodies with a somewhat lower strength, but still above 60 MPa, and water absorption of about 1.5% can be obtained upon the modification of clay with fly-ash (30%) and phonolite (40%). They also meet the specifications for chemical stoneware which has never been manufactured in Poland because the required parameters cannot be obtained using the traditional production technology.

The modification of clays not only brings definite technological effects but also makes it possible to save clay materials which are in short supply, and to utilize fly-ash and trachytic phonolite that has not yet found any application.

Translated by Hanna Kisielewska

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MODYFIKOWANIE WŁAŚCIWOŚCI TECHNOLOGICZNYCH ILÓW KAMIONKOWYCH DODATKAMI AKTYWNYMI W WYSOKICH TEMPERATURACH

Streszczenie

Iły przydatne do produkcji materiałów ceramicznych wypalone w określonej temperaturze powinny posiadać odpowiedni skład fazowy i teksturę. Szczególnie ważna jest zawartość mullitu, krystobalitu i kwarcu oraz fazy szklistej.

Podjęto próbę modyfikowania składu fazowego a tym samym właściwości ilów w stanie wypałonym wprowadzając do nich substancje mineralne, które w wysokich temperaturach są chemicznie aktywne i wchodzą w reakcje ze składnikami ilów. Mogą nimi być popioły lotne i skały bogate w alkalia. W stanie niewypałonym działają one schudzająco, podobnie jak kwarc, zmniejszając plastyczność i skurczliwość.

W pracy przedstawiono wyniki badań modyfikacji ilów kamionkowych z Łęknicy popiołem lotnym z elektrowni Turów i fonolitem z Opolna Zdroju w wysokich temperaturach.

Cel pracy zrealizowano w oparciu o technikę planowania eksperymentu. Założono, że charakterystykę matematyczną obiektu badań można aproksymować nielinową funkcją regresji rzędu drugiego. Obliczenie funkcji wykonano metodą analizy regresji z zastosowaniem EMC ODRA 1304. Ustaloną zależnością wybranych właściwości fizykochemicznych wypałonych ilów oraz zawartości w nich mullitu, kwarcu, krystobalitu i szkliwa od składników masy i temperatury wypałania.

Otrzymane równania regresji zinterpretowano graficznie. Wynika z nich, że ze wzrostem temperatury wypałania wzrasta ilość mullitu i szkliwa oraz spada wytrzymałość na ściskanie na skutek naprężeń na granicy faza krystaliczna-szkło. Wzrost ilości szkliwa wpływa w mniejszym stopniu na obniżenie wytrzymałości niż wzrost ilości mullitu w tworzywie. Przy dużej ilości szkła i wysokiej gęstości pozornej wzrasta wytrzymałość tworzyw.

Określono optymalny skład mas i temperatury wypałania dla uzyskania tworzyw o zwartej teksturze. Optymalne właściwości gwarantują masy z badanego ilu modyfikowanego fonolitem w ilości 20–40% lub popiołem lotnym (30%) i fonolitem (40%). Właściwości technologiczne wypałonych kształtek z tak modyfikowanego ilu odpowiadają najwyższej gatunkom kamionki kwasoodpornej.

OBJAŚNIENIA FIGUR

- Fig. 1. Dyfraktogramy próbki ilu z Łęknicy
 a — próbka orientowana, b — próbka po nasyceniu gliceryną, c — próbka po wyprężeniu w 600°C; K — kaolinit, I — illit, S — smektyt, MP — minerały mieszanopakietowe, Ch — chloryt, Q — kwarc, Kal — kalcyt, D — dolomit
- Fig. 2. Krzywe analizy termicznej próbki ilu z Łęknicy
 1 — próbka ilu naturalnego, 2 — frakcja <0,5 μm; warunki analizy = masa próbki — 800 mg, czułość TG-200 mg, DTA-1/10
- Fig. 3. Dyfraktogramy próbki fonolitu i popiołu lotnego z elektrowni Turów
 F-fonolit, P-popiół lotny; S-skalenie, Q-kwarc, M-mullit
- Fig. 4. Przykład dyfraktogramów służących do ilościowej analizy fazowej tworzyw ceramicznych XI–XII, XIV–XIV — numery mas według programu badań, M-mullit, Kr-krystobalit, Q-kwarc
- Fig. 5. Przykład dyfraktogramów służących do określenia ilości szkliwa w wypałonych próbkach ilów
 Q-kwarc, M-mullit, Kr-krystobalit
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МОДИФИРОВАНИЕ ТЕХНОЛОГИЧЕСКИХ СВОЙСТВ КЕРАМИЧЕСКИХ ГЛИН АКТИВНЫМИ ДОБАВКАМИ В ВЫСОКИХ ТЕМПЕРАТУРАХ

Резюме

Пригодные в производстве керамических материалов глины, после обжига в определенной температуре, должны иметь соответствующий фазовой состав и текстуру. Особенно важно содержание муллита, кристобалита и кварца, а также стекловидной фазы.

Предпринята была попытка видоизменения фазового состава, а тем самым свойств глин в обожженном состоянии, путем введения в них минерального вещества, которые в высоких температурах химически активны и входят в реакции с компонентами глин. Ими могут быть летучие пеплы и богатые в щелочи породы. В необожженном состоянии они действуют отощающим образом, подобно кварцу, уменьшая пластичность и усадку.

В работе представлены результаты исследований модификации высокотемпературных свойств керамических глин из Лэнкницы летучим пеплом из туровской ТЭЦ и фонолитом из Опольна-Здруя.

Цель работы достигнута была на основе техники планирования эксперимента. Заранее предположено, что математическую характеристику объекта можно аппроксимировать нелинейной функцией регрессии второго порядка. Расчеты функции проведено методом анализа регрессии с применением ЭВМ Одра 1304. Установлена зависимость некоторых физико-химических свойств обожженных глин, а также содержания в них муллита, кварца, кристобалита и стекла от компонентов массы и температуры обжига.

Полученные уравнения регрессии интерпретировались графически. Из них следует, что с увеличением температуры обжига растет количество муллита и стекла, а также уменьшается сопротивление сжатию вследствие напряжений на границе кристаллическая фаза-стекло. Увеличение количества стекла в меньшей степени влияет на уменьшение прочности, чем увеличение количества муллита в материале. При большом количестве стекла и большой кажущейся плотности увеличивается прочность материалов.

Установлены оптимальный состав масс и температура обжига для получения материалов компактной текстуры. Оптимальные свойства гарантируются массами испытуемой глины, модифицированной фонолитом в количестве 20–40%, или летучим пеплом (30%) и фонолитом (40%). Технологические свойства обожженных фасонных изделий так модифицированных глин соответствуют самым высшим сортам кислотоупорных керамических изделий.

ОБЪЯСНЕНИЯ К ФИГУРАМ

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 a — ориентированный образец, b — образец после насыщения глицерином, c — образец после обжига в температуре 600°C ; К — каолинит, I — иллит, S — смектит, MP — смешанные пакетные минералы, Ch — хлорит, Q — кварц, Kai — кальцит, D — доломит
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