INTENSIFIED HEAT TREATMENT OF COLLOIDAL CAPILLARY-POROUS MATERIALS

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Methods of investigating, improving, and intensifying the clay firing process are examined.

The broad intensification of the heat treatment (drying, firing) of colloidal capillary-porous materials is chiefly limited by their ability to resist heat.

In gas kilns, where heat is chiefly transferred by convection, high rates of flow of hot gas through the kiln zones are required to achieve high temperatures. Under these conditions, the temperature fields over the cross section of the kiln and the specimen are nonuniform. The nonuniformity of the temperature distribution (high gradients) frequently leads to potentially destructive temperature stresses and strains. Avoiding this is difficult, since gas kilns are not well adapted to automatic temperature regulation. The small working volumes of electric kilns make possible the stable maintenance of the necessary heating regimes and hence a considerable reduction in heat-treatment time.

The radiant heating technique in electric kilns favors the development of gradientless heating zones and correct firing conditions.

Clays and kaolins are fired at high temperatures. The principal object is to remove the gaseous components and obtain a product of different chemical composition with new mechanical properties.

During the drying process all the moisture, apart from the chemically bound moisture, is removed from the clay. P. A. Rebinder's classification of the forms of moisture binding is based on the degree of retention of moisture by the mineral. Most strongly bound is the chemical moisture (water of crystallization). It is removed at relatively high temperatures (550–650° C), whereupon the crystal lattice of the mineral kaolinite is destroyed and the substance metakaolinite with a new structure and properties is formed. The associated volume changes may involve unacceptable deformation and cracking which adversely affect the external appearance of the article and technical characteristics.

Our experimental automatic electric furnace [1] has enabled us to make a detailed study of the firing process and establish the principal causes of cracking.

To obtain the best possible product it is necessary to know the laws of heat and mass transfer throughout the process. In accordance with our method of investigation [2], the entire firing process was divided into three stages studied separately. This made it possible to improve the quality of firing and establish the optimum heating curve. At the very beginning of the investigation, to avoid destruction of the specimens, the heat-treatment processes (including drying) were carried out on the same apparatus. Thus we were able to avoid microcracks in specimens dried to constant weight. As the experiments revealed, when the drying and firing processes are separate, after drying in most cases the article absorbs moisture from the surrounding medium owing to its adsorption properties, which involves the formation of microcracks. Combining the two processes (drying and firing) in a single apparatus enabled us to improve the quality of the article and, by reducing the duration of heat treatment, accelerate the process. We found that in firing processes the most important stage is the dehydration period. Thus, in each individual case, depending on the properties of the material and the size of the specimen, a particular optimum heating regime is required. In the case of kaolinitic clays, the reduction of strength during the dehydration period is due to the destruction and reorganization of the crystal lattice of the kaolinite. Accordingly, they must be fired at relatively low heating rates and moderate temperature drops.

In accordance with the method of investigation developed, the heating conditions (from room temperature to 1000–1200° C) for these materials will be optimum if: 1) for specimens from 25 to 32 mm in diameter the

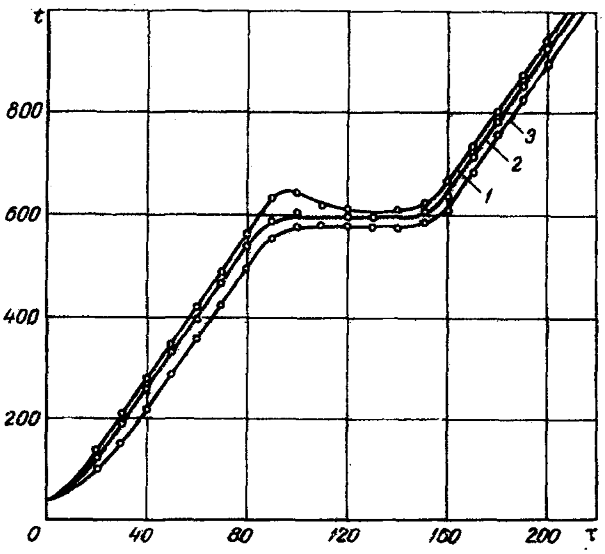

Fig. 1. Temperature graphs for the heating of a cylindrical specimen (D = 35 mm) of Prosyanovsk kaolin (t, °C; τ, min): 1) temperature of medium; 2) surface temperature of specimen; 3) temperature at center of specimen.

heating rate is 5–6 deg/min, the temperature drop between the surface and the center of the article 30–35° C. In firing specimens more than 35 mm in diameter, it is necessary during the dehydration period to go over to a regime with constant heating temperature (Fig. 1); 2) for specimens up to 25 mm in diameter the heating rate is 7–8 deg/min, the temperature drop up to 40° C.

After dehydration the strength and modulus of elasticity of kaolinitic clays increase with further heating.

In the case of refractory clay from the Chasov-Yar deposit, the phenomena associated with reconstruction of the crystal lattice during the dehydration period are less clearly expressed than in the case of kaolinitic clays. Accordingly, higher heating rates are permissible for this material. Thus, for example, specimens from 25 to 32 mm in diameter can be heated at rates up to 12 deg/min and temperature drops on the order of 40–45° C.

In firing specimens more than 32 mm in diameter it is necessary to go over to a regime with constant heating temperature during the dehydration period. For specimens up to 25 mm in diameter, a heating rate of 15 deg/min and temperature drops up to 50° C are permissible.

When a ceramic article is heated, a state of volume stress is created. If the thermal stresses exceed the strength of the material, it disintegrates. Therefore, we also calculated the criterion of crack formation, i.e., the mass transfer number Ki' for the most dangerous firing period. In the regular-regime stage, the curve representing the mass content kinetics is described by an exponential equation and the rate of mass loss of bound matter $d\bar{u}/d\tau$ is proportional to the average mass content of the body. Then the coefficient a' calculated from the formula

$$a' = \frac{R_1 R_2 (R_2 - R_1)}{(2.405)^2 \left(\frac{\bar{u}_2}{\operatorname{tg}\psi_2} R_1 - \frac{\bar{u}_1}{\operatorname{tg}\psi_1} R_2 \right)}$$

has the value $a' = 0.64 \cdot 10^{-4}\ \mathrm{m}^2/\mathrm{hr}$.

The coefficient a', which is expressed in the same units as the thermal diffusivity a, characterizes the inertial properties of the body with respect to propagation of the mass potential field.

The maximum rate of mass transfer, determined from the firing kinetics curve during this period, $q' = 1.609\ \mathrm{kg/m^2 \cdot hr}$. The specific mass content of the specimen $\bar{u}_0 = 0.1621$; the density of the fired specimen $\gamma_0 = 1800\ \mathrm{kg/m^3}$. From these data we determined the mass transfer Kirpichev number

$$\mathrm{Ki}' = \frac{q'R}{a' \gamma_0 \bar{u}_0} = \frac{1.609 \cdot 0.011}{0.64 \cdot 10^{-4} \cdot 1800 \cdot 0.1621} = 0.95.$$

As noted in [3], the Ki' number plays an important role in the technology of mineral heat treatment and can be used as a criterion of crack formation. Its range of variation is $0 < \mathrm{Ki}' < 2$.

The experimentally obtained value $\mathrm{Ki}' = 0.95$ corresponds to the most dangerous stage of firing from the standpoint of crack formation.

Consequently, the use of the above-mentioned permissible heating rates and temperature drops leads to an intensification of the firing process. At the same time, the stresses developed in the specimen do not exceed the permissible limits.

As our investigation has shown, the cooling period is also important. During intense cooling after maximum heating, owing to the large temperature drops between the surface and the center of the article and as a result of modificational changes in the body, internal stresses leading to deformation and even disintegration may occur. This is because on the temperature interval 1200–800° C the body undergoes a phase transformation accompanied by solidification of the glass phase. Accordingly, two-stage cooling was adopted as the safest procedure (Fig. 2).

On the temperature interval 1200–800° C the optimum cooling rate is 4–5 deg/min for Prosyanovsk and Glukhovetsk kaolins and up to 8 deg/min for refractory clay.

Slow cooling promotes the maturing of the body, i.e., the completion of all the liquid-phase reactions, which have a direct bearing on its mechanical characteristics. Cooling was intensified beyond 800° C (at 10 deg/min for kaolins and 15–16 deg/min for refractory clay). The reduction of the strength characteristics and the increase in water absorption of the test specimens at higher cooling rates were taken into account in our experiments.

The water absorption of the refractory clay was about 3% of its own weight (approaching 4% for Prosyanovsk and Glukhovetsk kaolins). These data indicate that the specimens were well fired.

The value obtained for the mass transfer Kirpichev number was higher than that given in [4]. Hence, our method of investigation opens up new possibilities for the improved heat treatment and intensified firing of minerals.

As already noted, the use of radiant heating ensures uniformity of heating and intensified firing. Therefore, electric furnaces are to be recommended for wide use in connection with the mass firing of individual articles, the organization of production lines and automation,

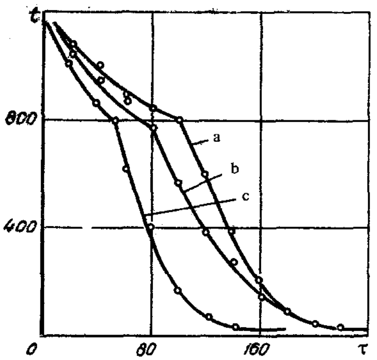

Fig. 2. Temperature graphs for the two-stage cooling of specimens of Prosyanovsk (a) and Glukhovetsk (b) kaolins and refractory clay (c).

and the firing of thin-walled articles to strict dimensional tolerances, when even brief temperature drops over the working space of the furnace are unacceptable. Moreover, electric furnaces have a number of other advantages over flame furnaces: accurate control of the temperature regime, total automation of the firing process, reduced percentage of rejects, noncontamination of the product, shortened heat-treatment times and, hence, intensification of the process, easy operation, improved working conditions, etc.

Consequently, in comparison with gas kilns, electric kilns permit the automatic regulation of various heating regimes (linear, combined) over a broad temperature range. Moreover, they are reliable and very economical. As noted in [5], starting only from the thermal equivalent (without taking the power plant efficiency into account), the heat consumed in firing glazed tile is, on average, for the Czechoslovak and American industries 5–6 thousand kcal per kilogram of product in open-flame gas kilns, 10–12 thousand kcal in gas muffle kilns, and only 2.5–4 thousand kcal in electric kilns.

Electric tunnel kilns with heaters made by the Kantal Company of Sweden are being widely used abroad. In Czechoslovakia an electric tunnel kiln with Kantal-Super heaters is being planned for firing steatite articles at 1400° C. The length of the kiln is 36 m, the annual output 900 tons, the installed power 250 kW [6].

Similar kilns with Kantal-Super heaters have been introduced in Yugoslavia, West Germany, and Finland for producing carborundum wheels, domestic porcelain, and electrical ceramics, respectively [6]. Electric tunnel kilns are usually on a small scale. For example, the Siemens-Plania kiln, intended for firing at temperatures up to 1400° C, has a cross section of 0.15 m^2 and a total length of 13.5 m. These small volumes make it possible to maintain a stable firing regime, thus considerably reducing the firing time. As far as possible kilns should be inertialess. Thus, for example, the heaters are exposed inside the kiln.

The widespread introduction of electric kilns in the ceramic industry should increase the quality of production, facilitate the work and reduce the number of the operating personnel, and cut costs.

To summarize, the optimum heating regimes proposed are designed to intensify the firing process, shortening its duration to 2–3 hr, i.e., by approximately 50% in comparison with ordinary production conditions.

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