Influence of capillary autohesion on structure and molding properties of ceramic granular molding compounds

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Abstract. The prerequisites of optimal designing of compositions of raw mixtures for the production of molded ceramic products, based on the laws of the formation of polydispersed structures, is presented in the paper. The choice of methods for calculating the optimal humidity of raw mixtures, providing the optimal parameters of their compacting is suggested. The influence of the humidity of the raw mixture on the packaging of its particles and bulk density, as well as the plastic strength of the molding, taking into account the action of capillary adhesion, is shown in the article.

1. Introduction

The formation of the structure of the raw material mixture, which is largely inherited in the structure and properties of finished products, is influenced by the autogenesis of powder particles. Autohesion is a strong interaction between the contacting particles and is determined by the breaking strength of the contact between them. Autohesion is the sum of forces of different nature, namely the strength of the molecular interactions (Van der Waals forces, and cohesion), electric forces, capillary forces and mechanical cohesion. The autohesion of a certain powder material can be caused by the action of several forces simultaneously. Mutually exclusive are only the electric and capillary forces [1-3].

Autohesion in technological processes has both positive and negative effects. In cases where it is necessary to reduce the dispersion of powders or prevent delamination of the powder mixture, autohesion has a positive effect. At the same time, in the mixing processes the homogeneity of the mixture can be significantly disturbed as a result of the formation of aggregates [2, 4-6, 8, 9]. Powers of autohesion contribute to caking, and the formation of arched structures, the formation of bridges at the outflowing of powders from bins and other containers [2, 5-7, 10-13].

The study of the influence of autohesion of powder materials on the structure and properties of the raw material mixture in the technology of molded ceramic products is an important task to optimize the formation of the mixture and the technology itself. This is explained by the fact that the technological ways of processing, storage and transportation of the raw material mixture, as well as the molding of products are widely used in the production of not only ceramics, but also refractories, concretes, composite materials of different purposes, biomaterials, electronics, food and cosmetics, and everywhere the significance of the forces of autohesion is proven [2, 6, 14].

Structure formation in disperse systems is the result of forces of inter-partial interaction: intermolecular, electric, capillary. Although a large number of studies are devoted to the study of particle adhesion (autohesion) in disperse systems, specific issues related to the type of structural elements and structures as a result of the dominant role of capillary adhesion forces in the structure...
formation have not been considered in detail until recently. Just as the structures formed as a result of coagulation are called coagulation, the structures formed as a result of the action of the capillary bond forces, we proposed to call capillary [15].

2. Materials and methods
Experiments were carried out on dry molded ceramic powder to produce tiles. The chemical composition of the sample of the molded powder is shown in table 1.

| Table 1. The chemical composition of the ceramic molded – powder. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SiO$_2$         | Al$_2$O         | Fe$_2$O         | CaO             | MgO             | R$_2$O$_3$      | ppp             |
| 59.56           | 19.8            | 1.0             | 2.44            | 2.19            | 6.26            | 8.39            |

The grain composition of the molded powder was determined using a set of sieves with cell sizes: 1 mm; 0.5 mm; 0.25 mm; 0.1 mm. According to the sieving of the molded powder, private residues were calculated as a percentage equal to the ratio of residues on these sieves to the total weight of the sample, which was 200 g, as well as total residues in percentage equal to the sum of private residues on these sieves and on sieves with large cell sizes. Table 2 shows the granulometric composition of the molded powder used in the work.

| Table 2. Granulometric composition of the ceramic molded powder. |
|-----------------|-----------------|-----------------|
| The cell size of the sieve, mm | Private residue, % | Full residue, % |
| 1               | 0.025           | 0.025           |
| 0.5             | 1.325           | 1.35            |
| 0.25            | 63.375          | 68.725          |
| 0.1             | 25              | 93.725          |

Table 2 shows that about 70 % of the molded powder has pellet sizes from 0.25 to 0.5 mm. Technological properties of the molded powder are its bulk density, flowability and angle of natural slope. The bulk density was determined by the known method, which consists in filling a cylindrical glass with a capacity of 50 cm$^3$ from a funnel with a hole diameter of 15 mm. The funnel was installed 10 cm above the upper edge of the glass, and thus 150 g of molded powder was poured through the funnel into the glass. After filling the glass with the formation of excess molded powder in the form of a cone, it was cut level with the edges of the glass without compacting the molded powder.

The bulk density of the molded powder in terms of dry matter (g/cm$^3$) was calculated by the formula

$$\rho_u = \frac{m_1 - m_2}{50 \left(1 + \frac{W}{100}\right)},$$

where $m_1$ – mass of the vessel with the molded powder, g; $m_2$ – mass of the vessel, g; $W$ – moisture of the molded powder, %.

For determination of porosity of separate granules and molded powder as a whole in this work a special technique is proposed. As you know, the porosity or voidness of the bulk material (%) is determined by the formula

$$\Pi = \frac{\rho - \rho_u}{\rho} \cdot 100,$$

where $\rho$ – true density, g/cm$^3$; $\rho_u$ – bulk density, g/cm$^3$.

The true density of the molded powder was measured using the Le Chatelier-Candlo volume meter. Since the granules of the molded powder in the water disintegrated into tiny particles, the volume of
the displaced liquid in the volume meter was almost equal to the absolute volume of the ceramic substance that makes up the granules.

The volume of granules together with pores was determined in the same volume meter when it was filled with kerosene. The powder before filling was moistened to 10 %, which is approximately equivalent to filling the pores in the granules with water. Since water and kerosene are mutually immiscible and immiscible liquids, wet granules in kerosene retained their shape and displaced kerosene by an amount numerically equal to its volume along with internal pores. According to the above humidity, the sample of the molded powder poured into the volume meter was counted on the dry substance, and the ratio of the latter to the displaced volume of kerosene was taken for the density of the granules of the molded powder.

The porosity of the granules (%) is calculated by the following formula

$$\Pi_g = \frac{\rho - \rho_r}{\rho} \cdot 100,$$

where \(\rho\) – density of the granules of the molded powder, g/cm³.

The intergranular porosity (voidness) of the molded powder in the freely poured state (%) is determined by the formula

$$\Pi_{mg} = \frac{\rho - \rho_n}{\rho} \cdot 100.$$

The total porosity of the molded powder in the compacted state is calculated by a formula similar to (2), only instead of \(\rho_n\), the average density of the compacted molded powder \(\rho_o\) is substituted in this formula.

In experiments to study the effect of the moisture content of the molded powder on its properties and compaction, additional moistening of the molded powder was carried out by pulverization. After moistening to separate a small number of lumps, the molded powder was passed through a sieve of 1.25 mm. In order to obtain a moisture content less than natural, the molded powder was dried in room conditions.

3. Research result

The data on the bulk density in terms of dry matter of the ceramic molded powder spray drying are shown in figure 1. For comparison, the same figure shows the data obtained when measuring the bulk density of the same molded-powder from moisture by tilting at an angle of 60° gutter, set the update above vessel at 10 cm bulk density of molded powder in both cases with the increase of humidity decreases owing to formation of aggregates of granules and an increase in intergranular voidness molded powder as a result of capillary autohesion.

Figure 1 shows that the values of the bulk density of the molded powder depend on the method of its measurement. Therefore, the use of data obtained in the laboratory, when calculating the actual conditions of filling the molded powder in the mold molded is possible only after studying these conditions and their modeling. At the same time, this characteristic of the molded powder cannot be measured in the first way (through the funnel) at a humidity level of the molded powder more than 16% because of the strong clumping, and to identify the relation in the entire humidity range, it is necessary to use the gutter. In this case, the minimum bulk density of the molded powder is found at a humidity of about 17 %, then the bulk density of the molded powder increases sharply.

The results of measurements of flowability and the angle of natural slope of the molded powder with a change in humidity from 2 % to 15 % showed that these characteristics are little dependent on humidity in the specified range and are respectively 45-46 g/s and 20–22° [16].

The values of the bulk density of the molded powder, the density of its granules, as well as the intergranular porosity (voidness) of the molded powder and the porosity of the granules at the original density of the ceramic substance of 2.52 g/cm³ are given in table 3.
The calculated data show that the porosity of the granules is about 30% of the total porosity of the molded powder in a free bulk state. This indicator is an important characteristic of the molded powder, reflecting its microstructure, while the bulk density of the molded powder, which characterizes the macrostructure, depends primarily on the grain composition of the molded powder.

![Figure 1. The relation of the bulk density of the molded powder on the dry matter upon the humidity in the measurements with the funnel (1) and the gutter (2).](image)

**Table 3.** The values of the bulk density of the molded powder, the density of its granules, as well as the intergranular porosity (voidness) of the molded powder and the porosity of the granules.

| Humidity of molded powder $W_0$, % | $\rho_b$, g/$\text{cm}^3$ | $\rho_g$, g/$\text{cm}^3$ | $P_i$, % | $P_g$ % |
|----------------------------------|------------------------|----------------------|--------|--------|
| 0                               | 0.85                   | 1.80                 | 52.8   | 28.6   |
| 4.8                             | 0.813                  | «                    | 54.8   | «      |
| 7.7                             | 0.805                  | «                    | 55.3   | «      |
| 10                              | 0.792                  | «                    | 56.0   | «      |
| 16                              | 0.785                  | «                    | 56.5   | «      |

According to the granulometric composition of the molded powder according to the method [16, 17], the volume-surface diameter or the weighted average size of the granules is determined:

$$d_{3,2} = \frac{\sum g_i}{\sum g_i d_i}$$  \hspace{1cm} (5)

where $g_i$ is the fraction of granules with diameter $d_i$, %, by weight; $d_i$ is the average size for the partial residue of the molded powder, mm.

The values of the volume-surface diameter of the granules of the molded powder and the porosity of the granules in various samples of the molded powder (table 4) show that there is a certain
correspondence between these values, namely, the porosity of the granules decreases as the size of the granules decreases, which is confirmed by the literature data [17].

**Table 4.** Volume-surface diameter and porosity of the granules of the molded powder in various samples and fractions.

| Probe numbers | Volume surface diameter of powder, mm | Granule porosity, % | Fraction, mm | Granule porosity, % |
|---------------|--------------------------------------|---------------------|--------------|---------------------|
| 1             | 0.281                                | 29.9                | 1–0.5        | 33.2                |
| 2             | 0.303                                | 32.9                | 0.5–0.315    | 33.0                |
| 3             | 0.298                                | 31.4                | 0.315–0.25   | 30.6                |
| 4             | 0.299                                | 32.9                | 0.25–0.1     | 25.8                |

Figure 2 shows the relation of the shear stress limit determined by the penetration rheometer PRB-2 [18] on the moisture content of the molded powder at different density of the samples after molding: 0.95; 1.0; 1.05 and 1.1 g/cm³. The data show that with increasing humidity, the values of the shear stress limit, as well as the value of the capillary coupling in these systems, increase, reach a maximum at a certain humidity $W_{mc}$, and then decrease.

Figure 2. Ultimate shear stress of the molded powder depending on the humidity at different density of the molded samples: 0.95 (1); 1.0 (2); 1.05 (3) and 1.1 (4) g/cm³.

From the theory of capillary adhesion, it follows that capillary autohesion between two spherical particles has the largest value at the time of the formation of a liquid meniscus in the zone of their contact. It is obvious that the meniscus between the granules of the molded powder is formed after filling their pores with moisture. Calculate the moisture content of the $W_{mc}$ molded powder corresponding to this point by the formula
\[ W_{mc} = \frac{\Pi_g \cdot \rho_w}{\rho_r}, \]  
\[ \text{где } \rho_w - \text{密度 of a liquid phase (water), 1 g/cm}^3. \]

Substituting the values of \( \Pi_g \) and \( \rho_r \) given in table 3, we obtain a value of \( W_{mc} \), equal to 15.9 %, which is satisfactorily consistent with the experimental data (see figure 2).

Thus, the capillary coupling, which is the basis of the strength of the freshly molded semi-finished product, has a maximum value at a certain humidity, the value of which can be calculated by the formula (6).

The relation of the density of the molded powder in the compacted state on the humidity (figure 3) shows that with increasing humidity of the molded powder its density increases, reaches a maximum at a certain humidity, and then decreases.

**Figure 3.** Relations of density of a molded powder in the condensed state on humidity at molding pressures: 1 – 10 MPa; 2 – 20 MPa; 3 – 30 MPa.

In figure 3, the dashed line corresponds to the critical humidity, where the system at a given molding will have a two-phase state and a maximum density. In the two-phase state of the system, all pores are saturated with water. Until this condition when the humidity increases the density of the molding powder when molding increases. These dependencies differ from dependencies of apparent density of moulded powder (see figure 1), features-soumise a low bulk density and a relative humidity close to the value \( W_{mc} \).

These differences are explained by the fact that with free backfilling with an increase in humidity to the specified humidity corresponding to the maximum capillary adhesion, an increase in the aggregation of the molded powder under the action of capillary autohesion occurs, while when compacting the molded powder from plastic clay raw materials, the reduction of internal friction between the particles with the preservation of autohesion bonds is of decisive importance.

Molding of ceramic powders at mouldedures adopted in the production of ceramic products, the critical humidity values are 1.5–2 times less than the moisture content of the \( W_{mc} \). Thus, the system achieves the maximum density long before the humidity (\( W_{mc} \)) at which the capillary adhesion can
reach its maximum and that is manifested in the case of dependencies of the bulk density of the molded powder. Therefore, under the actual conditions of molding ceramic molded powders it is necessary to determine the critical values of humidity, which correspond not only to the maximum possible compaction of the molding, but also to the maximum possible value in the given conditions of capillary adhesion. These humidity values are also the best for increasing the strength of finished products [19].

4. Conclusion
Molding the raw material mixture of optimal humidity contributes to the restructuring of the microstructure of the mixture, primarily by reducing the number of macropores and increasing the strength of the contact zones, as well as the average density of molding. At the same time, the strength of ceramic products with an optimal structure will be maximum, which will ensure a decrease in the energy consumption of products and an increase in their quality indicators.

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