Modification of clay raw materials to optimize slip casting

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Abstract. The effect of surface-active substances (surfactants) on the state of water in clay was studied based on the data of swelling and sedimentation of clay particles in aqueous suspensions. The features of the influence of three types of additives - technical lignosulfonate and hyperplasticizers manufactured by Arkema and Movecreate are considered. When surfactant solutions are introduced into the clay system, an increase in the wettability of clay particles is observed, which promotes the adsorption of surfactant molecules on the surface of the dispersed phase, which depends on the structure of clay minerals and their impurities. Surfactants simultaneously have a plasticizing and structuring effect on the clay mass, leading to intensification of drying in the initial stages and, consequently, to a decrease in shrinkage deformations. The most effective additive is lignosulfonate, the introduction of which in an amount of 0.01 % in a clay suspension increases the fluidity of the suspension, and the mobility of water decreases by more than 3 times than in the presence of hyperplasticizers. The best preservation of the suspension is also ensured in the presence of a plasticizer - lignosulfonate. The main difference in the action of polycarboxylates and lignosulfonate is to change the sedimentation rate of clay suspensions. Modification of clay loam by surfactants leads to improved drying properties, quantified in a decrease in sensitivity to drying.

Keywords: clay raw materials, slip casting, surfactants, wettability, sedimentation.

1 Introduction

There are several basic methods for molding ceramic products from clay raw materials. The main ones are the method of "plastic" molding and the method of semi-dry pressing. The "slip casting" method also finds application. The choice of the method of molding raw determines both the mineral composition of clay raw materials and its career moisture. So, raw materials from bentonite clay raw are usually molded by the method of plastic molding, and kaolin by slip casting. In addition, the type of ceramic product also makes its own adjustments. So, for example, the basis for ceramic tiles, even from red-baked raw materials, is molded in a semi-dry way. In this case, the press powder is obtained by wet grinding of the slip followed by spray drying. Slip drying stage is accompanied by high energy consumption, which is desirable to minimize. One of the ways to use energy-saving technologies can be the use of surface-active substances (surfactants) that change the structure of water, as shown previously [1-4]. The effectiveness of surfactants in the plastic molding method was shown in [5]. There was an improvement in the formability of the mass and drying properties of the raw material. Data on the effect of surfactants on the features of slip casting are insufficient, and it is in these technologies that it is most important to evaluate the interaction of clay particles with water. The rheological and thixotropic properties of clay suspensions are regulated by the introduction of deflocculants [6–8], which are mainly used as sodium salts, and can replace surfactants. An analysis of the properties of plastic and movable slips [9] showed the prospects for the transition to a skinny slip, for the possibility of complicating the injection molds of modern design.

Thus, the work is devoted to assessing the influence of surfactants and the state of water in a clay slurry. In addition to the ability to control the properties of the slip itself, using a surfactant, it is possible to reduce the water content in the casting suspension, lowering the cost of spray drying.

2 Materials and methods

At the first stage, the swelling ability in water was determined - one of the main indicators of the quality of clay raw materials. A measure of swelling ability is the increment of a certain amount of...
clay when interacting with water. The experiments were carried out on two types of clays, significantly differing in the degree of swelling: clays of the Yaush field and Nurlat-Oktyabrsk bentonite. Both loams are semi-acid, moderately plastic clay raw materials. The main clay mineral of the loam of the Yaush field is mixed-layer illite-smectite (23 %), Nurlat-Oktyabrsk is bentonite. For testing, clay samples were closed with distilled water (or distilled water containing surfactants of various nature in amounts from 0.01 to 0.1 %). The lignosulfonate and the Arkema and Movecreate carboxylate hyperplasticizers were used, which are related to ionic surfactants and have a slightly acidic environment. Lignosulfonate belongs to polyanionic surfactants - natural water-soluble sulfonic derivatives of lignin. Movecreate and Arkema polycarboxylates are comb-like water-soluble carboxylate polymers. Arkema polycarboxylate is a grafted copolymer of acrylic polycarboxylate and polyethylene glycol stabilized with sodium chloride, doped with 0.1 % CNTs (carbon nanotubes). The state of the resulting suspension was monitored for 5 days. The retention time of the suspension (sedimentation time) was determined and the degree of swelling was controlled by the change in the average particle size. The particle size in suspensions was evaluated according to a HORIBA LA-960 laser analyzer. The viscosity of clay suspensions was estimated by the expiration time on a VZ-246 viscometer. The effectiveness of the modification of clay suspensions by slip technology was established by the following parameters: fire shrinkage, the density of the raw material and the crock, as well as the compressive strength of the crock.

3 Results and discussion

With the introduction of surfactants, the distribution of clay particles in size becomes bimodal. For an example in Figure 1 are presented data for clays of the Yaush field.

The ability of water-soluble macromolecular compounds to aggregate colloidal particles, discovered by V. Anri, leads to the interaction of dispersed phase particles through molecules adsorbed on their surface surfactants (flocculation phenomenon) [9,10]. This explains the increase in sediment increment after sedimentation while reducing the average particle size in modified clay suspensions.

The results of the measurement processing are given in table 1. The degree of swelling for the original clay is much higher than with the modification of surfactants (a larger increase in the size of clay particles is observed). A decrease in swelling ability in a weakly acidic medium is a characteristic behavior for clays [11-16]. It turns out that the increment in the height of the sediment after the end of the separation for the original clay is less. The process of separation begins faster in the presence of a surfactant (2 and 5 minutes, respectively, in the presence of Movecreate and Arkema), and in the case of lignosulfonate begins only in 1.5 hours, and complete sedimentation occurs in 5 days.
Table 1. Characterization of clay suspensions.

| Clay            | Additive     | Surfactant content, % | Conditional viscosity, (nozzle 4, initial state), sec |
|-----------------|--------------|-----------------------|------------------------------------------------------|
| Yaush Source loam |              | 0.01 % Lignosulfonate | 12.67 13.44 17.63 10 745 |
|                 |              | "+" 0.01 % Movecreate | 11.21 12.01 12.92 40 7300 |
|                 |              | "+" 0.01 % Arkema     | 10.52 13.11 13.76 2 412 |
| Source loam     |              | 0.10 % Movecreate     | 12.78 11.16 14.47 5 512 |
| Nurlat-Oktyabrsk|              | 0.10 % Arkema         | 17.73 16.63 14.64 47 2270 |
|                 |              | 0.01 % Lignosulfonate | 13.15 13.46 15.55 60 7700 |
|                 |              | "+" 0.01 % Movecreate | 15.4 14.18 15 27 1620 |
|                 |              | "+" 0.01 % Arkema     | 15.39 14.94 15.79 34 1870 |

Since the viscosity of a clay slip, which depends on the degree of interaction of the particles of the dispersed phase, plays a role for subsequent drying processes of products during molding, experiments were carried out with different surfactant contents (0.01 % and 0.1 %). Viscosity measurements were carried out immediately after preparation of the slurry and after 30 minutes of exposure. The data are presented in table 2.

Table 2. Clay slurry viscosity.

| Clay      | Additive     | Surfactant content, % | Conditional viscosity, (nozzle 4, initial state), sec |
|-----------|--------------|-----------------------|------------------------------------------------------|
| Yaush     |              | 0.01 % Lignosulfonate | 21.30 23.08                                           |
|           |              | "+" 0.01 % Movecreate | 22.80 24.92                                           |
|           |              | "+" 0.01 % Arkema     | 23.21 26.49                                           |
|           |              | "+" 0.01 % Movecreate | 15.97 16.37                                           |
| Arkema    |              | 0.10 % Lignosulfonate | 40.53 does not expire from the nozzle                  |
|           |              | "+" 0.01 % Movecreate | 28.03 does not expire from the nozzle                  |
|           |              | "+" 0.01 % Arkema     | 16.92 17.65                                           |
The introduction of lignosulfonate leads to a decrease in the conditional viscosity of the clay suspension. Lignosulfonate is an ionic surfactant, which molecules are adsorbed on the faces of crystals of clay particles in the created slightly acidic medium [17-20]. Active groups of lignosulfonate molecules capable of structuring water find themselves inside spheroidal aggregates. The resulting structure improves the sliding of particles with respect to each other and water molecules, causing the slip to thin. A similar effect of reducing the apparent viscosity was noted in [21], where the effect of low viscosity carboxymethyl cellulose (CMC) on the suspension of talc as a deflocculant was shown. Polycarboxylates (Arkema, Movecreate), on the contrary, are characterized by the formation of hydrogen bonds in the side chains of vaccinations. When these molecules are adsorbed onto clay particles, provided that it is possible to form intermolecular hydrogen bonds in the side chains of the combs of adjacent molecules, coagulation of the suspension occurs, causing the slurry to thicken. Over time, at sufficiently high concentrations of surfactants (more than 0.1%), a complete loss of fluidity is observed. A similar increase in the viscosity of modified clay suspensions is explained by the structural features of polycarboxylate molecules, which side chains can limit the mobility of clay particles due to the formation of hydrogen bonds.

Changes associated with the interaction of modified clay suspensions in the system are due to changes in the state of water in the presence of surfactants [2]. Molecular mobility of water in the presence of lignosulfonate has been shown to stall more than 3 times compared to hyperplasticizers. As a result, lignosulfonate leads to a greater degree of ordering of water molecules than polycarboxylates, which affects the interaction of modified water molecules with clay particles. In modified clay suspensions there is a decrease in mobility compared to the pure clay suspension, and in the presence of lignosulfonate non-uniformity of decline is detected, which indicates different degree of connectivity of water molecules in the suspension composition.

The adsorption of surfactants from solutions to the surface of clay particles and impurities in the composition of clays, primarily depends on the wettability. In [2], as an example of two types of low-melting loam, it was shown that the wettability of clay particles in the presence of surfactants improves and it is concluded that in the slip, the adsorption of surfactants occurs primarily on the surface of clay particles, rather than impurities.

Based on the developed suspensions containing 0.01 and 0.1% surfactants, samples were obtained by slip technology, which were fired according to the regimes similar to plastic molding technology. Plasticizing additives were previously introduced into the mixing water in order to obtain a homogeneous solution. The test results of the samples are given in table. 3 by the example of clay of the Yaush field.

Peculiarities of structure formation during slip drying lead to the fact that the destroyed structure of the clay mass as a result of clay dissolution in the aqueous solution is not able to self-compact without external efforts, and the increased water content during drying helps to reduce the density and strength of the samples during slip molding. However, it can be seen from the data in Table 3 that the presence of only 0.01% lignosulfonate allows to reduce the shrinkage value and practically maintain the strength characteristics.

| Indicator (firing at 1000 °C) | 50% clay of the Yaush field + 50% distilled water | 0.01% Arkema | 0.10% Arkema | 0.01% Movecreate | 0.10% Movecreate | 0.01% lignosulfonate | 0.10% lignosulfonate |
|------------------------------|-----------------------------------------------|---------------|---------------|-----------------|---------------|---------------------|---------------------|
| Fire shrinkage, %            | 5.2                                           | 5.8           | 5.0           | 6.2             | 4.3           | 4.6                 | 6.5                 |
| Raw Density, kg/m³           | 1507                                          | 1542          | 1523          | 1499            | 1508          | 1523                | 1467                |
| Shard density, kg/m³         | 1647                                          | 1621          | 1572          | 1595            | 1583          | 1560                | 1579                |
| Compressive strength, MPa    | 25                                            | 19            | 23            | 20              | 20            | 26                  | 26                  |

Table 3. Properties of samples made by slip method.
4 Conclusion
The use of surfactants of various nature can regulate the fluidity of a clay suspension, which is important in the slip technology for manufacturing ceramics. It has been shown that the effectiveness of surfactants depends on the chemical nature and concentration. So, the use of LST in an amount of 0.01% can significantly improve the slip fluidity, increase the sedimentation time up to 4 times and up to 10 times before the start of separation. It has been established that the adsorption of surfactant molecules proceeds mainly on clay particles, thereby setting the rheological parameters of the slip can be achieved with lower water content, which will result in lower energy consumption at the drying stage in energy-intensive spray dryers.

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