Features of the preparation of calcium-containing raw materials in the production of ceramic bricks

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Abstract. The paper considers possibility of using low-melting loam, drilling waste and ash and slag waste of thermal power plants in the production of wall ceramics by the method of semi-dry pressing. The physicochemical processes occurring upon receipt of ceramic materials using production waste at the firing stage are studied. It has been established that an increase in the duration of grinding of calcium-containing raw materials at the stage of preparation of the starting materials determines a change in its particle size distribution, an improvement in the plasticity of the molding materials and an increase in the coherence of the raw product and provides an increase in the mechanical strength of the raw product in comparison with the initial indicators.

1. Introduction

Ceramic wall products are of particular interest due to the complex of physical and mechanical indicators, Environmental friendliness and architectural expressiveness. The stability of production technology and the receipt of final products with desired properties determine the increased need for high-quality raw materials. However, the limited development of conditioned clay deposits in the Russian Federation, the significant costs of its extraction and transportation force enterprises to abandon imported high-quality raw materials and use local clays in production, as a rule, characterized by low plasticity and the presence of various impurities in them, and corrective additives including industrial waste.

For regions where industrial production and processing of solid and liquid fuels is developed: coal, gas, oil, it is urgent to solve the problem of utilization of ash obtained from the combustion of coal when it was previously used in boiler houses, waste from drilling wells characterized by multi-tonnage (more than 25,000 tons / year ). For the storage of this type of waste, it is necessary to arrange dumps and sludge pits, which increases environmental pollution and requires additional land resources.

In connection with the foregoing, in the context of constantly increasing prices for the development, extraction of prior raw materials and their transportation, energy sources one of the main tasks in the building materials industry is the introduction of resource-saving, energy-efficient technologies in the production of building ceramics. This determines the relevance of the research topic - the study of the features of preparing calcium-containing raw materials in the production of ceramic bricks that meet the requirements of GOST R 52108-2003, based on local widely distributed raw materials.
low-melting clay raw materials - loams and mineral constituent waste from drilling wells during oil production (hereinafter referred to as MOB) and ash slag waste (hereinafter ASW).

2. Materials and methods
The starting materials are clay from the Buguruslan deposit, the mineral component of drilling waste from the facilities of PJSC Orenburgneft, and the ash and slag waste of the Orsk TPP. The chemical composition of the raw materials is presented in table 1.

| Clay deposit | Chemical composition (oxide content), mass. % | loss on ignition |
|--------------|---------------------------------------------|-----------------|
|              | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | K₂O | Na₂O | SO₃ |
| Buguruslan   | 60.44 | 13.53 | 10.46 | 3.35 | 2.81 | 2.92 | 2.99 | -   | 3.50 |
| MOB          | 28.45 | 4.06  | 3.56  | 43.6 | 4.96 | 4.50 | 0.68 | 9.22| -   |
| ASW          | 29.28 | 8.66  | 3.65  | 3.75 | 1.24 | 0.31 | 0.94 | -   | 44.45|

According to the content of alumina in terms of the calcined substance, the feedstock belongs to the group of sour; the content of iron oxides (Fe₂O₃ > 3 %) is characterized by a high content of coloring oxides. The low content of Al₂O₃ in the waste indicates its fusibility, which in the MOB is enhanced by the presence of a greater amount of alkaline oxides in comparison with the ASW. Alkaline-earth oxides are present in all types of experimental raw materials - in a smaller amount in the ZHO and Buguruslan clay (the total content of CaO and MgO oxides is 7.1 and 4.05 %, respectively) and there is an increased content in the MOB (ΣCaO, MgO = 48.56 %), which indicates the presence of carbonate impurities. Petrographic and X-ray diffraction analysis confirmed the presence in the clay and industrial waste in a uniformly distributed finely divided form of carbonate compounds: calcite, dolomite, which can lead to lime and various brick defects resulting from firing.

3. Results
The behavior of the feedstock during heat treatment was studied. The results are presented in Figure 1.

The analysis of the obtained results confirms the fusibility of the experimental raw materials and allows attributing the MOB and ASW to the group of raw materials with an extended sintering interval. These results indicate the possibility of using experimental types of industrial waste in the production of ceramics as modifying additives in compositions with loam of the Buguruslan deposit.

At the first stage of research, during the pressing, drying, and burning of samples, the factory modes were used, which subsequently changed. The compositions of raw materials obtained previously experimentally [1, 2] were dosed according to the experimental design, wt. %: Loam (95-45) + MOB (or ASW) (5-55), moistened (W-form = 10 %), aged for 1 day in a desiccator and molded on a press with a pressure of 20 MPa c holding for 30 seconds. Drying was carried out at a temperature of 120 °C to a constant humidity of 3 %. Firing was carried out at a temperature of 1100 °C with exposure at a maximum temperature for 240 minutes. The results obtained for a bicomponent mixture of composition: loam of the Bugurslansky field + MOB is shown in Fig.2. Similar results were obtained for the mixture of composition: loam of the Bugurslansky field + ASW.

According to the results of the studies, it was found that the introduction of MOB / NW in the selected range to the masses from the loam of the Buguruslan deposit leads to a decrease in Rcr by 24 / 17 %, respectively. At the same time, the water absorption of samples on the Buguruslan loam with the addition of MOB increases from 13.8 to 16.3 %, with the addition of ash and slag clay - from 11.32 to 23.2 %.
Thus, the samples of the experimental compositions with technogenic additives after firing are characterized by relatively low mechanical strength under compression and loosening of the structure, which, according to the authors, is explained by:

- structural changes associated with an increased content of carbonate compounds and the decarbonization reaction occurring during the firing process;
- low reactivity of MOB and ASW particles;
- high voidness of press powders that do not provide a snug fit of particles during pressing.
The increased content of carbonate inclusions in the feedstock with a grain size of more than 0.32 mm, according to the author of [3], can lead to the formation of cuts in the samples. One way to solve this problem is to grind the raw material to a particle size of less than 0.032 mm in diameter [4]. In the process of fine grinding of carbonate-containing material, its particles, decreasing in diameter, are activated, impurity iron oxides turn into nitrous oxide. These changes accelerate the onset of the reaction with silica and contribute to the formation of silicates and complex spinels [5].

It was established in [6] that an increase in the reactivity of press powders can be achieved by reducing the particle size and increasing the defectiveness of the crystal structure of the minerals that make up the ceramic mixture. It should be noted that molecular-dense aggregation, along with the destruction of the lattice, makes it impossible to identify a direct relationship between the dispersion and the chemical reaction of press powders [7].

In connection with the foregoing, the influence of the grinding time on the change in the grain composition of a two-component charge and on the activation of sintering of a raw product in the temperature range of 950 - 1200 °C was investigated.

For fine grinding of mineral raw materials, vibration, planetary and centrifugal ball mills are widely used in the production. The intensification of mechanical dispersion is achieved only by increasing the work of grinding media, the mass of which should not change during the whole process. This condition provides high dispersion, a particle shape close to spherical and close contact between particles necessary for solid-phase interactions.

During the experiments, a laboratory ball mill was used to grind the raw materials. Uralitic balls are used as grinding bodies. During the experiment, dry grinding of the raw materials of the mixture was carried out in two stages, as a result of which the influence of the grinding duration on the dispersion of the feedstock was determined. Initially, a dosed loam was loaded into the ball mill drum. The grinding time was 50% of the total duration. Then, after batching the MOB, it was added to the ball...
mill and joint grinding of the components was carried out. The percentage of different fractions after
grinding was determined by the method of Rutkovsky. The results of studies of the change in the ratio
of particles of clay, sand, and dust fractions depending on the grinding time are presented in Figure 3.

![Figure 3](image)

**Figure 3.** Change in the particle size distribution of raw materials based on loam of the Buguruslan
deposit depending on the grinding mode and type of calcium-containing additive: 1 - ASW in quantity
30 %; 2 - MOB in quantity 30 %.

Analyzing the data obtained, it was found that an increase in the duration of grinding of masses
based on loam of the Buzuluksky deposit with technogenic additives up to 120 minutes leads to an
increase in the number of clay and dust particles. In the granulometric composition of the «loam of the
Buguruslan deposit + ASW» charge, the content of clay particles increased by 59.18 %, of dusty
particles by 40.67 %, the content of sand particles decreased by 57.05 % with respect to the 30 minute
duration of grinding of the masses.

Mechanical processing of the initial components of the mixtures based on loam of the Buguruslan
deposit and the MOB allowed increasing the content of clay particles by 63.7 %, dust particles by
28.2 %, the content of sand particles decreased by 58.7 %, the dispersion of the experimental masses
relative to the original raw materials, past grinding for 30 minutes respectively, 46.9 % and 44.12 %.

However, an increase in the amount of clay and dust particles and a decrease in the amount of sand
particles are noted when grinding the components for 30 to 120 minutes. With an increase in the
duration of grinding the experimental masses to 150 minutes, the amount of clay particles decreases
and the content of dusty and sand particles increase.

The results of the studies made it possible to establish the interval of change in the diameter of the
particles of the charge «Buguruslan loam + ASW» with a grinding time of 150 minutes – 2-700
microns, with a grinding duration of 90 minutes – 0.85 - 600 microns. A similar dynamics of the
distribution and change in the quantitative content of particles was obtained for a crushed two-
component mixture based on loam of the Buguruslan deposit with the addition of 30 % MOB
depending on the grinding time: 1 – 700; 0.8 - 550 microns.

The results obtained are consistent with the authors’ opinion [8, 9] that brittle fracture of a solid
occurs during the grinding of mineral raw materials, leading, in particular, to a change in the state of
the surface of the loam and MOB / ASW particles and the development of irreversible plastic
deformations of the surface layers. As the particle size decreases, they harden and then aggregate;
decrease in the energy of grinding media due to the appearance of viscosity in finely ground substances. As a result of changing conditions, the rate of destruction becomes equal to the rate of aggregation and the dispersion process stops.

On samples molded by semi-dry pressing from two-component press powders with different grinding times of the raw materials and the resulting particle size distribution, the change in the technological parameters of the raw product was studied (Figure 4).

![Figure 4. Change in the particle size distribution of raw materials based on loam of the Buguruslan deposit, depending on the grinding mode and type of calcium-containing additive: 1 - ASW 30%; 2 - MOB 30%.](image)

From the results of Figure 4 it can be seen that with an increase in the grinding time of raw materials with calcium-containing additives from 30 to 120 minutes, there is a general tendency to improve the ductility of molding materials (based on ASW / MOB by 94.6 and 77.4 %, respectively), and the grinding time is longer significantly affects the increase in the plasticity of the masses initially with a lower value for ASW, and the mechanical strength of the raw product similarly increases (based on ASW / MOB loams by 86.51 and 67.87 %, respectively).

### 4. Conclusion

Thus, the results obtained allow stating that:

1. The increase in the duration of grinding of the feedstock for 150 minutes is impractical, since it leads to an increase in the formation of particles of dusty and sand fractions in the masses on the basis of loam of the Buguruslan deposits, respectively, for ASW / MOB with the addition of 30 % by 10.13 and 9.87 / 4.1 and 9.87 %, a decrease in the amount of formation of particles of clay fractions by 34.8 / 36.4 %, an increase in the voidness of further obtained press powders, as a result of which, upon subsequent pressing of products, defects appear in its structure - cracks, delamination with ressovannogo products - raw.

2. The duration of the grinding of the charge components for 120 minutes makes it possible to obtain in the future the optimum specific surface area of the press powder particles 2380 - 2450 cm²/g, the grain composition of the molding mass provides pressing of the raw material without defects with the highest density and mechanical strength.
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