Modeling an Increase in the Cement Activity Using Dispersed Mineral Additives

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Abstract. The researches’ results show that it is possible to obtain a ceramic crock, which water absorption meets the requirements of facade ceramic tiles at a charge firing temperature of 1150 °C, consisting of 60% low-melting and 40% refractory clay raw materials from deposits in the Novosibirsk Region. Additives influence nature of directed action was studied: wollastonite and cullet by the mathematical planning method of the experiment. It was found that the introduction of additives helps to improve the physical and mechanical properties of the ceramic crock. The introduction of 10% cullet allows increasing the tensile strength by 10.3% compression and reducing water 27.1% absorption. The amount of 15% wollastonite contributes to a greater increase in mechanical strength and a decrease in water absorption, compared with the control composition. The joint introduction of mineral additives leads to a decrease in tensile strength A method for producing high-quality facade and building ceramics from low-grade, poor in clay minerals raw materials with carbonate inclusions, which consists in mechanically activating these raw materials and purposefully creating a hierarchical structure of semi-dry pressed products, is proposed in the research work. The developed technology of preparing a press-mass that is uniform in humidity and dispersion by rolling mechanically activated powders based on aggregate grains (micro level), firmly coated with clay mineral nanoparticles, to the state of spherical granules (macro level). This approach to mass preparation significantly improves the subsequent stages course of pressing and firing products. Its effect is the possibility of obtaining various types of building and facade ceramics with high performance characteristics.

1. Introduction

Ceramic wall and building materials are structured as composites consisting of a matrix, which is a product of high-temperature transformations of clay minerals, and aggregate (sand and other rock-forming minerals). The ratio of their volume fractions is determined by size distribution and aggregate grains packing. The fraction of free space between them is 25.95% in the close packing case of identical spherical grains [1]. This value is the theoretically necessary volume fraction of the matrix to completely fill the voids between the filler grains. Its value increases for disordered packages. The space between filler particles will not be completely filled, filled with a binder consequently, in cases where clay minerals in the feedstock are in amounts significantly less than this threshold value (~26 o6.%). Moreover, its distribution in these voids will be uneven, if traditional technologies of mass preparation...
are used by mixing the components. The composite structure will be archaic, the matrix will be porous, with broken connectivity, and as a result the products strength will naturally decrease [2]. Ceramic masses have unsatisfactory rheological properties for the production of plastic molding products, based on such raw materials poor in clay minerals. This explains the low interest in Siberian loesslike loams containing less than 26% (usually 10-12%) [3] clay minerals, as raw materials for the production of high-quality facade ceramics by plastic molding, so a semi-dry pressing method is often recommended [4].

In practice, ceramic wall materials have a stochastic, conglomerate type of structure, obtained by semi-dry pressing [5]. Its heterogeneity is due to the technological methods’ peculiarities of raw materials’ mass preparation and press powder molding, which currently leads to the production of low quality products. So, the main disadvantages of semi-dry pressing plants in Russia are: rough grinding of raw materials (maximum size up to 3-4 mm); low quality of press mass (inhomogeneous particle size distribution, fluctuations in fractional humidity, etc.); outdated pressing technology on mechanical presses (volumetric dosing, and as a result, different pressing pressures in the molds) [6]. These shortcomings of this process are a serious obstacle to its full automation, which is relatively easily implemented in plastic molding plants. Thus, in order to obtain high-quality facade and building ceramics from Siberian loesslike loams, it is necessary to substantially review all the technological stages of its production - from mass preparation to firing. First of all, the semi-dry method for the production of ceramic products must be brought to a qualitatively new technological level.

1.1 Theoretical background
The ceramic material strength depends on the specific strength of the contacts between its grains and the area of these contacts. Therefore, It is necessary to use such mass preparation technologies that lead to an increase in the specific surface of the contacts an increase in their number per unit volume of the composite, as well as an increase in the specific strength of these contacts in order to prevent the loss of composite materials strength, caused by deficiency of a binder (in our case, clay component). In our opinion, these technologies should ensure the achievement of the following results in comparison with traditional:

1) at the grinding stage

- fine grinding of mineral raw materials, especially potential binders (clays, hydromica minerals and feldspars) and fluxes (carbonates);
- uniform coating of binder and smooth surface of the filler grains with microparticles, so that the binder always appears in the contact area between the filler grains. With such a core-shell type, the particles’ microstructure of a binder press powder is less than 26 vol. % when the ratio of the shell thickness to the grains diameter of quartz is less than 0.05, as it follows from the analysis of the ideal composite packing [1];
- an increase in the reactivity of the filler and binder particles to ensure their sufficiently strong adhesion, which would allow heteromineral particles, organized as a core-shell, to be preserved during subsequent technological operations with the prepared powder mass,

2) in the preparation of the molding material

- "assembly" of heteromineral powder particles into closely packed homogeneous aggregates of sufficiently large size, which would contribute to uniform filling of the molds and unhindered removal of air during compression molding of the press mass,

3) at the stage of drying and firing pressed products

- the absence of drying defects, associated with the heterogeneity of the press mass in terms of moisture and grain size;
lowering the temperature of phase transformations for the filler microparticles, which would ensure the proper sintering depth during the firing and hardening process.

In addition, this technology must be inexpensive, economical and environmentally friendly.

Thus, a new mass preparation technology is needed that allows one to radically change the physicochemical state of the raw materials mineral particles, and subsequently the morphology of the press mass in order to achieve a high quality of ceramic products with clay minerals below the threshold value (26 vol.%). This technology should provide highly dispersed powders with a high concentration of various surface and bulk defects in their particles. An essential requirement is also the organization of these powders’ specific microstructure, which have quartz grains as their main component, coated with thin layers of binders and fluids.

In our opinion, the mechanical activation of loams most closely meets the above requirements in paragraphs 1-3. In order to use this method, the required dispersion of the powders (<100 μm) is achieved, the surface microroughness and the particles defectiveness of these powders components are increased. Some chemical processes are intensified, already under grinding conditions, such, as dehydration of hydroxides or crystalline hydrates and solid-phase acid-base reactions [7].

The mechanical activation of polymineral powders in a fluidized bed in vortex-mill-dryers causes triboelectrification of their particles. Minerals usually acquire surface charges opposite in sign, that differ greatly in their acid-base properties (for example, metal and non-metal oxides), in terms of mechanical strength or ability to absorb water vapor [8]. Ultimately, triboelectrification can lead to self-organization of these particles into complex aggregates due to Coulomb interactions: for example, a coating of clay binder flakes should be expected to form on the surface of the filler particles in the case of loams. Moreover, the strength of its adhesion, obviously, will be determined mainly by electrostatic forces, and at the final stage also by chemical interaction during mechanochemical activation at the initial stage of this coating formation.

As a result of decreasing the minerals’ particle sizes and the accumulation of volumetric and surface defects in these particles, their reactivity always increases. According to “Big Chemical Encyclopedia” for small particles the relative change in the phase transformation temperature is determined by the expression:

\[-\Delta = T \cdot Td = \left( \frac{\sigma V_m}{H_{ph,t}} \right) \frac{\partial s}{\partial v}\]

where T and Td – phase transition temperatures, respectively, for bulk and dispersed (activated) substances, respectively; σ – surface tension; Vm – molar volume of substance; Hph,t – phase transition enthalpy; s – surface and v – substance particle volume. Derivative \(\frac{\partial s}{\partial v}\) is determined by the particle’s shape and inversely proportional to its size.

The effect of temperature lowering in the phase transition is most pronounced for nanoparticles with a size of 1-5 nm (500-100 °C), which production is hardly possible in significant quantities under the conditions of usual mechanical activation, however, the appearance of sharp chips, scratches, cracks, protrusions, i.e. sites with small radii of curvature on the surface of the minerals’ micro particles, may cause their surface melting under firing conditions.

Consequently, the reaction sintering of their particles during products firing will be intensified due to the morphological and microstructural features of the powders, and the formation of thin glass-like layers from high-temperature products of its interaction with the clay shell is quite likely on the surface of the filler (quartz particles, etc.).

In its turn, a material with volume ratio between matrix and filler, that entire matrix contained in surface films is absent in the “free” state, has a pronounced non-additivity of properties. This is due to the fact that the substance of the matrix, changes its properties, including mechanical ones, being in the surface layer under the adhesion forces action. The increased dispersion and micro-roughness of the filler grains in such material is a factor, causing the growth of the cracks’ surface fractal during its mechanical failure, which contributes to its hardening [9]. All these structural features of ceramic
products, obtained from mechanically activated loams, will contribute to the improvement of their operational properties, such as mechanical strength, frost resistance, etc.

However, there are problems that seem insoluble in the case of the generally accepted technologies of bricks and tiles semi-dry pressing. So, finely dispersed powders demonstrate a rather low ability to close packing after mechanical activation [10-11]. The presence of trapped air, filling powders reduces the accuracy of their volumetric dosing during pressing, which ultimately affects the quality of the molded product.

To eliminate these problems, it would be advisable to introduce an additional procedure - obtaining dense aggregates from heteromineral particles of these powders (the requirement in paragraph 2.), immediately before pressing the product. In principle, this is achievable with granulation of powders by intensive aggregation: capillary forces created by liquid films, and multidirectional impact deformations of the resulting granules will lead to compaction of their internal structure. As a result, the molding of products from such granules by pressing will be reduced to volumetric plastic deformation of the granules layer filled into the mold, and the air outlet from the spaces between the granules will be facilitated due to the sufficient size of the gaps between them.

This work demonstrates the approaches to mass preparation and pressing proposed, it is possible to obtain a variety of high-quality facade and building ceramics from Siberian loess-like loams that are generally unsuitable for this within the framework of traditional methods.

2. Materials and Methods

The clay raw materials of the Berdsky deposit (Novosibirsk region) were used in the work. It belongs to loess-like loams, siltstone-sandy and finely dispersed. According to x-ray phase analysis (XRD), its mineral composition includes 50-70 wt. % quartz, 5-10 wt. % carbonate minerals, 10-20 wt. % feldspars and 12-14 wt. % clay minerals. We used granular foamglass-crystalline material “Kerwood” of 0.6-1.2 mm fraction, as a macro-filler for effective ceramic composites of a hierarchical structure (LLC STEP-Invest, Chelyabinsk).

The mechanical activation of the feed was carried out in a vortex-type drying and grinding plant, where drying and selective grinding were carried out in a fluidized bed of a coolant [12]. In this installation, selective grinding of the raw material took place with its simultaneous drying at 250-300 °C, as a result, soft rock-forming minerals (clay, carbonate) were crushed to a size of less than 100 microns. After grinding, the moisture content of the raw material was 3-4%, the powder residue on a 0.2 mm sieve was 10-15%.

Granulation of mechanically activated powders was carried out in a turbo-pad mixer-granulator manufactured by Dzerzhinsk technomachine, in order to obtain granules of predominant size 2-3 mm with a moisture content of 8-10%.

The ceramic products were molded on a SM-1085 press at a specific pressure of 15-18 MPa, drying and firing were carried out in a tunnel furnace; the firing temperature was 1000 °C.

The morphology and microstructure of the press powders’ particles was studied by transmission electron microscopy (TEM) using a JEM-2010 instrument (accelerating voltage of 200 kV).

The microstructure of the shard sections was examined using a PPM-8 polarizing mineralogical microscope, and the surface texture of the shards was examined by scanning electron microscopy (SEM) using the JSM-6460LV device (accelerating voltage 15-20 kV).

The diffraction patterns were recorded using a URD-6 diffractometer (CuKα radiation). Samples were scanned by points (signal accumulation time 5 sec) with a step of 0.05 ° in the range of angles 2θ =15-90°.

Frost resistance, strength and water absorption of products were determined according to SST 530-2012.

3. Results

Morphology of mechanically activated loam particles. Micrographs of mechanically activated loam, obtained by TEM (Figure 1) show that relatively large particles are surrounded by a “coat” of small
fragmented particles. These are hetero-mineral conglomerates organized by the shell-core type. Quartz grains act as nuclei. The shells, surrounding them, are formed from nanoscales of kaolinite-hydromica micas and finely divided feldspar inclusions, and their sizes are less than 0.2 microns. It was previously shown these minerals both, worn out to nanosized particles and also accumulated many structural defects and microstresses in their volume, as it was evidenced by a change in the ratio of reflex intensities and their broadening in diffraction patterns of milled samples during mechanical activation [1].

Figure 1. Microphotographs of loam after mechanical activation.

It turned out that heteromineral conglomerates do not decompose in the aquatic environment even after prolonged ultrasonic processing and quickly precipitate from the suspension together with quartz, while free-dispersed particles of the clay component settle much more slowly, creating a separate sediment layer. This indicates that the minerals’ particles in the conglomerates are connected with the surface of quartz grains and with each other, both mechanically and also through chemical bonds, thus forming a kind of network for quartz microcrystals.

The mechanism of the heteromineral conglomerates formation during the mechanical activation of loam is most likely, based on the phenomena described of the powder particles triboelectrification during grinding and their self-assembly under the influence of Coulomb forces with subsequent relaxation of surface defects and chemical bonds formation between the particles.

3.1. Formation and properties of mechanically activated clay loam ceramics
Granulation and pressing. Granules with a size of 2-3 mm and a moisture content of 8-10% are obtained as a result of activated powders aggregation in a turbopaste granulator. The reason for such a low need for press powders during granulation, and subsequently low sensitivity of raw brick to drying, is most likely the microstructure of their particles, where quartz grains are coated with partially dehydrated clay minerals in the form of durable shells, which are not destructible (and slightly swelling), wetted with water.

In the process of pressing products, the surface of the granules themselves is enriched with colloidal particles of clay minerals due to the diffusion of moisture from the central part of the granules’ body to the periphery [13]. As a result, in the places of granule contact, the condensation-crystallization structures turn into coagulation, which ultimately leads to a change in the character of
the ceramic composite sintering by the type of plastic molding. The resulting raw product has the characteristic structure of densely packed polyhedral, after pressing (Figure 2).

Thus, it was possible to achieve the unique case, when the dispersion of the components and their microstructure are such cases, that a filled one is enclosed in thin surface layers of the other, which is a binder through mechanochemical activation of the feedstock. In its turn, large dense aggregates are formed, as well as the particles composing them, coated on the outside with a thin layer of a binder during the granulation of such a dispersed powder. After pressing the resulting granules, it is possible to form an ordered bulk structure of the raw material at the micro and macro levels, as a result, it can be attributed to the type of hierarchical structures.

![Figure 2. Fragment of the raw brick structure from granular press powder.](image)

Firing. Layers of clay minerals and fills covering the surface of quartz particles and rounded granules turn into a glassy mass tightly fastening the encapsulated aggregate grains into a single frame at the firing stage at 1000 ° C, (Figure 3, 4). From these figures it can be seen that the obtained material is fine-grained of 40-50 microns in diameter and insignificant porosity at their boundaries. In a similar manner, the granule shells also sinter with each other. These features of the crock microstructure are the high activity result of granular press powders, which make possible the rapid occurrence of various reactions between their components during the firing of products.

It follows that the crock, obtained during firing, preserves the hierarchical structure of its raw predecessor, considering figures 3 and 4. Thus, the hierarchical structure of the final ceramic composite arises due to the targeted formation of the ordered structure of the press masses at the micro and macro levels during grinding (mechanical activation) and granulation.

Physico-mechanical characteristics of ceramic bricks, obtained by semi-dry pressing from rounded granules of mechanically activated loam, are given in table 1. It is obvious that the operational characteristics significantly exceed those for factory products, obtained by the traditional technology of mass preparation of press powder, including drying of raw materials in a drying drum, coarse grinding (up to 3-4 mm) and homogenization in a core mixer.

3.2. The formation of effective ceramics from mechanically activated loam as a binder

The mechanical activation of Siberian loesslike loams opens up wide opportunities for obtaining various types of ceramic products with an ordered structure. For example, it is possible to obtain an effective ceramic brick with a high volume content of porous or organic aggregate using a semi-dry method [14], which is often impossible with plastic molding due to an insurmountable deterioration in the rheological properties of the moldable mass.
Figure 3. The surface texture of the cleaved ceramic shards (according to SEM). A glass-like shell is visible around the aggregate grains.

Figure 4. The surface structure of a ceramic crock’s thin section in passing (a) and polarized (b) light. Brick-red color shows fused shells of clay minerals around grains of quartz (micro level) and granules (macro level of the hierarchical structure of the crock).

Table 1. Physico-mechanical characteristics of semi-dry pressed products from mechanically activated loam (1) in comparison with the factory charge (2).

| method | Tensile strength at | Average density, kg/m³ | Water absorption, % | Frost resistance cycle. |
|--------|---------------------|------------------------|---------------------|------------------------|
|        | MPa compression      | MPa bending            |                     |                        |
| 1      | 19.34               | 2.56                   | 1875                | 10.56                  | 50                     |
| 2      | 12.08               | 2.22                   | 1770                | 13.64                  | 25                     |

It is easy to obtain a mixture with a filler content of up to 50%, based on its industrial production (Table 2) [sixteen] it is possible to produce an effective brick with a strength grade of M150, using a new method of activation mixing finely dispersed activated loam powder with granular foam glass material “Kerwood”.

Studies of the structure and phase composition of ceramic bricks, based on granular foam glass-crystalline material and activated loam using petrography, scanning electron microscopy (SEM) and
X-ray diffractometry showed that closed round pores with a vitrified surface are formed (rice 5-6), firing at the site of HPSC granules

**Table 2.** Physico-mechanical characteristics of ceramic bricks based on mechanically activated loams with porous aggregate “Kerwood”.

| Tensile strength at compression MPa | Tensile strength at bending MPa | Average density, kg / m³ | Thermal conductivity, W / (m × °C) | Water absorption, % | Frost resistance cycle |
|-----------------------------------|--------------------------------|--------------------------|------------------------------------|---------------------|------------------------|
| 16.22                             | 2.22                           | 990                      | 0.21                               | 7.08                | 50                     |

There is a pronounced melted layer with a thickness of 30-100 μm, which is a solid spherical waterproof shell with a glass crystal structure at the interface between the solid and the gaseous medium. In the process of firing at a temperature of 850-900 °C, the shell of foam-glass-crystalline granules goes into a pyroplastic state. The formed liquid phase lines the inner surface of the macropore, which arose at the site of granule due to the partial pressure forces of heated gas phase and surface tension of the liquid phase inside the granule. The resulting boundary between the gas phase of the closed macropores and the solid phase of ceramic skeleton is represented by a glass-crystalline mass, where the relict minerals fragments of quartz and feldspar are melted and partially dissolved [15].

**Figure 5.** Semi-dry pressed ceramic brick was obtained by activation mixing mechanically activated loam with granular foam glass material “Kerwood” (section).

**Figure 6.** SEM image of the brick microstructure is shown in Figure 5: 1 - closed pores formed at the place of filler from GPSSM; 2 - ceramic frame made of loam; 3 - glassy pore boundary.
4. Discussion
A method for the production of wall (façade) ceramics, based on mechanically activated loess-like loams with a high concentration of carbonate impurities, is proposed. As a result of mechanochemical activation, a specific microstructure of the powder is achieved, consisting of quartz grains coated with finely dispersed particles of clay minerals for a press mass of semi-dry pressed production with the help of granulation on a turbo-mixed granulator-mixer.

The described approach to the molding material preparation, makes it possible to obtain ceramics of high density and strength due to the hierarchical structure creation of the crock, along with its high activity in solid-phase reactions in the process of the products firing, where the compressed granules are sintered with each other due to the formation of a glass crystal shell from products of thermal clay transformation minerals, which also forms around the aggregate grains, consolidating them inside the granules themselves.

Thus, the mechanochemical activation of low-grade raw materials, poor in clay minerals, provides a fairly simple and economical way to produce high-quality building and wall (façade) ceramics of bricks and tiles.

It is important that the use of mechanochemical activation technology in the preparation of press masses does not require significant changes in goods production by the method of semi-dry pressing. The main technological operations are carried out simultaneously in one unit - in a drying-grinding installation of a vortex type, usual for the traditional scheme of semi-dry pressing (drying of raw materials, then grinding and homogenization). In addition, the screening stage, required by the traditional technology of semi-dry pressing, is eliminated. The number of technological crossings is reduced. An additional operation is the preparation of granular press masses homogeneous in humidity and fractional composition, which can be implemented on turbo-blast granulator mixers manufactured by Dzerzhinsk technomachine in Russia. The obvious advantage of the proposed method also lies in the fact that it is effective, using low-grade raw materials, which significantly expands the raw material base for the production of high-quality wall and building ceramics in the Siberian Federal District.

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