

## Increase in frost resistance of a ceramic brick from clay raw materials of the Atyukhtinsky field

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**Abstract.** The present article reveals the results of the fulfilled research on increase in frost resistance of a ceramic brick from clay raw materials of the Atyukhtinsky field by means of semi dry molding. Based on the analysis of published sources, it has been established, that the most effective way to increase frost resistance of ceramic brick is an injection of different structuring additives into clay mass, which provide obtaining necessary characteristics of the porous structure of the material – a high content of reserve pores in the brick. In the function of an additive we have tested calcium-containing secondary products – wastes, extracted during the production of phosphate mineral fertilizers. The carried out researches demonstrate that the injunction of calcium-containing additive into clay mass with preliminary plastic preparation and following granulation leads to formation of optimal porous structure of ceramic brick and, consequently, to increase in frost resistance.

The modifying additive effect on the porous properties, when examining the sample, was defined by the fact that due to the additive injunction volumes of total and opened porosity in burnt ceramic samples increased. The additive did not affect significantly on capillary and closed porosity. The amount of reserve porosity of burnt ceramic samples increased 2 times with using of waste products. Because of this, frost resistance increased from 4 cycles (samples made from pure clay raw material) to 152 cycles (samples with additive). X-ray diffraction analysis showed that the rise in crystal phases content (anorthite and helenite) is an increase cause of strength of samples containing the additive.

It should be mentioned that the injunction of the additive in the already prepared molding powder, made according to the traditional technology (drying of the raw material and its grinding less than 3 mm) did not lead to a significant change in physico-mechanical indices of samples. It has been determined that the significant increase of frost resistance occurs only when injecting the additive during preliminary plastic preparation of clay mass with the following granulation – a little dried raw clay material ground less than 1 mm, mixed with the additive, after that grains 15mm in diameter were extracted from wetted mass and then ground less than 3mm.

In such a manner, the use of the modified calcium-containing additive in the molding batch composition and thereby achieved characteristics of the received products confirm the fundamental possibility of producing lining frost resisting ceramic brick of semi dry molding, as is evidenced by the results of carried out researches and pilot-scale tests.



## 1. Introduction

The current problem of the construction engineering industry development is wall materials durability increase, the substantial proportion of which is occupied by ceramic brick. Ceramic wall materials have always been basic materials for constructing walls due to their architectural expressiveness, simplicity and mass production, raw materials base availability, as far as for their production it is possible to use not only traditional clay raw material, but also various production wastes [1-9].

The paramount significance in the ceramic materials durability assurance, maintenance of mechanical strength under pressure, bend and other physical-mechanical characteristics of constructions is attributed to solving the problems of ceramic products frost resistance. The usage of high frost resistance materials in building construction industry allows ensuring a long term of service of such constructions at minimum expense.

A large amount of brick factories existing today in Russia were built in the Soviet period (until the 90's of the 20<sup>th</sup> century) and many of them are working according to the technology of semi dry molding. As the practice reveals, it often happens so that the brick of semi dry molding is inferior to the products of soft-plastic molding in terms of frost resistance.

It is widely-known that frost resistance depends on porous structure of material. The porous structure of ceramic products, as it is determined [10-12], in many aspects depends on material, grain-size composition and other natural properties of ceramic raw materials, as well as on the production technology, presence of the defined set of clayprocessing facilities, the way of pressing and the method of firing of products.

Nowadays frost resistance increase methods have a definite number of drawbacks and don't always contribute to frost resistance increase of brick. The increase in frost resistance of brick of semi dry molding can be achieved by technical re-equipping, substitution of outdated or installment of supplemental equipment improving the quality of preparation and homogeneity of raw material, enhancing drying and burning schedule and providing a higher level of technological bounds. This requires great material and financial expenditures which are not always reasonable or available due to the limited access to financial resources.

The transition to the raw clay material of a higher quality also raises expenses on transportation and storage. On injecting fuel-bearing (pore-forming) additives into clay mass it doesn't necessarily lead to the frost resistance increase, there can appear dark stains on the surface, thereby such products would not meet the requirements of lining brick surface appearance.

The increase of temperature during the firing sometimes doesn't improve the quality of the brick depending on the properties of the raw material.

During the production of items by means of semi dry molding, on the stage of pressing airbrick, there forms a coarse-pored structure where almost all pores come into contact with the atmosphere. And for high frost resistance, as it is known, in products there should be reserve pores, unreachable for water in normal conditions of humidifying [10]. Such pores are reservoirs for driving surplus moist on its migration during freezing products. This gives an opportunity to decrease internal pressure in the material and maintain ceramic brick intact.

In relation to the written above, the most effective way to increase frost resistance of ceramic brick is an injection of different structuring additives into clay mass, which provide obtaining necessary characteristics of the porous structure of the material.

In the function of an additive we have tested calcium-containing secondary products – wastes, extracted during the production of phosphate mineral fertilizers. These wastes are white disperse powder with the size of grains mostly 30-100 mkm. Chemical composition is represented in table 1.

**Table 1.** Results of chemical analysis

| Name of material                            | SiO <sub>2</sub> Free quartz | Chemical composition, % |                                |                                     |       |      |                      |                  |                  |                   |                               |        |
|---|------------------------------|-------------------------|--------------------------------|-------------------------------------|-------|------|----------------------|------------------|------------------|-------------------|-------------------------------|--------|
|   |                              | SiO <sub>2</sub>        | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> gen. | CaO   | MgO  | SO <sub>3</sub> gen. | TiO <sub>2</sub> | K <sub>2</sub> O | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | p.o.i. |
| Raw clay material of the Atyukhtinsky field | 28.73                        | 58.76                   | 10.26                          | 5.62                                | 8.51  | 2.86 | 0.03                 | 0.70             | 1.14             | 2.03              | -                             | 9.78   |
| Waste products                              | -                            | 0.68                    | 1.04                           | 0.44                                | 45.97 | 2.13 | 4.00                 | 0.13             | 0.01             | 0.03              | 0.99                          | 44.08  |

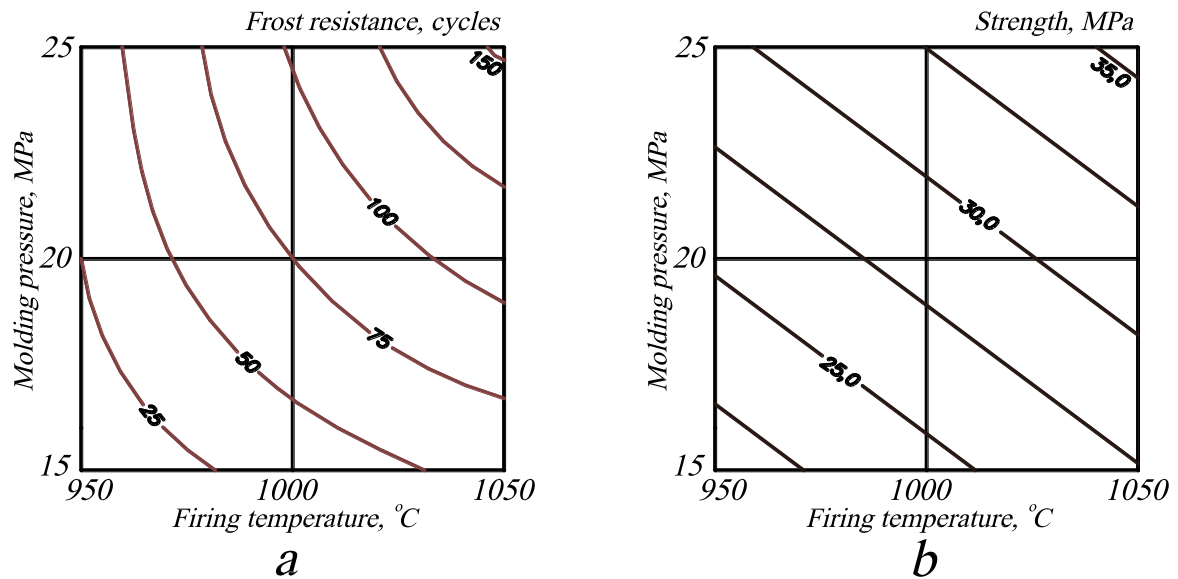
The present article deals with the results of the research on the influence of the given additive on the frost resistance of the ceramic brick produced from the raw material of the Atyukhtinsky field by means of semi dry molding. The given raw material is a quiet typical type of material for brick production in the South of Russia. The raw material from the Atyukhtinsky field according to its plasticity index is referred to the group of moderately plastic clay raw material, according to its sensitivity to drying it is highly sensitive (according to the method of A.F. Chizhsky). The chemical composition represented in Table 1 allows referring the material to the group of acidic clay raw material with a high content of coloring oxides, according to the degree of fusibility – nonsintering (brick water absorption is more than 5%), according to its fire resistance – low-melting, it is characterized by the majority of clay minerals of montmorillonite hydromicaceous type.

As a result of the carried out research, it has been discovered that products made from clay raw material of the Atyukhtinsky field by means of semi dry molding appeared to be frost-susceptible. The injunction of waste products in the 5%- mass allowed raising the index of frost resistance significantly (table 2). The abovementioned optimal proportion was defined by earlier fulfilled researches [13, 14] and gives an opportunity to achieve high indices of strength and frost resistance.

**Table 2.** Physico-mechanical characteristics of fired samples

| Mass composition, %                          | Firing temperature, °C | Strength, MPa  |            | Water absorption, % | Frost resistance, cycles |
|--|------------------------|----------------|------------|---------------------|--------------------------|
|  |                        | On compression | On bending |                     |                          |
| Clay raw material - 100                      | 1050                   | 24.1           | 6.1        | 13.2                | 4                        |
| Clay raw material – 95<br>Waste products - 5 | 1050                   | 35.7           | 8.5        | 13.7                | 152                      |

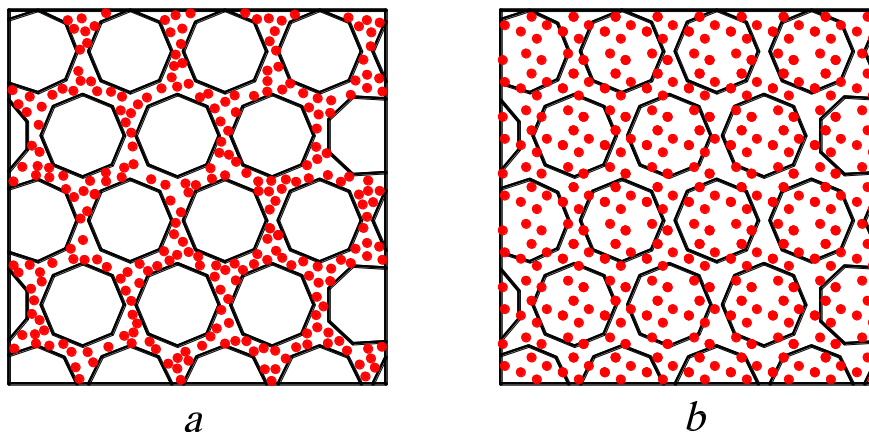
The research of unit area pressure and firing temperature influence according to mathematical method of planning experiment has shown (figure 1) that the frost resistance for more that 50 cycles is possible to achieve on molding pressure 20-25 MPa and firing temperature 1000-1050 °C.



**Figure 1.** Influence of molding pressure and firing temperature on frost resistance, cycles (a) and strength of samples on compression, MPa (b)

It should be mentioned that the injunction of the additive in the already prepared molding powder, made according to the traditional technology (drying of the raw material and its grinding less than 3 mm) did not lead to a significant change in physico-mechanical indices of samples. It has been determined that the significant increase of frost resistance occurs only when injecting the additive during preliminary plastic preparation of clay mass with the following granulation – a little dried raw clay material ground less than 1 mm, mixed with the additive, after that grains 15mm in diameter were extracted from wetted mass and then ground less than 3mm.

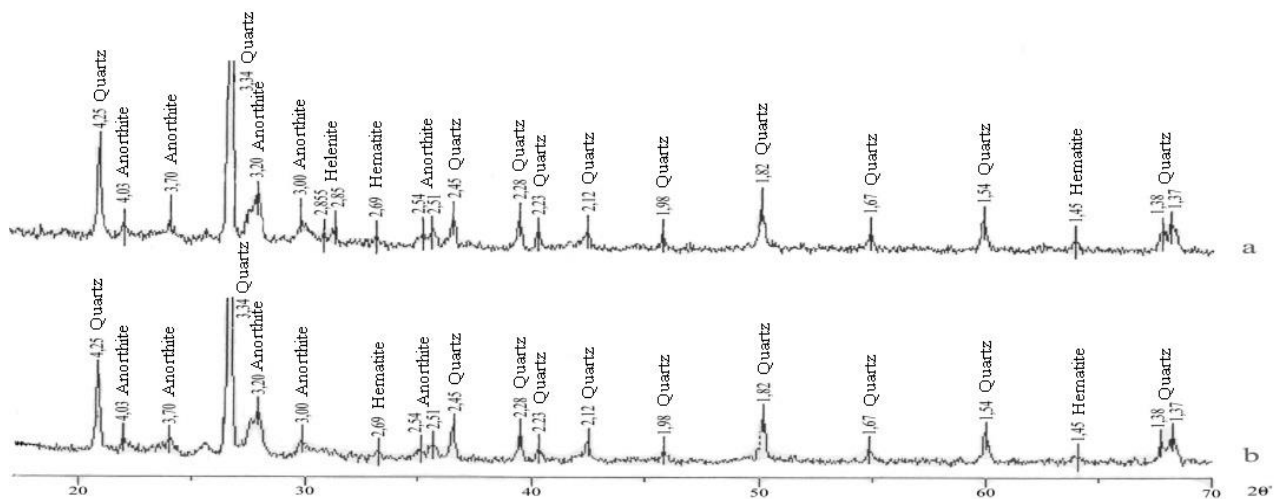
It appears that without any preliminary plastic preparation of clay mass, we can observe disperse additive powdering of bigger clay grains that contributes to worsening of sintering process and lowering of frost resistance of ceramic brick (figure 2).



**Figure 2.** Distribution of the additive in molding powder in the traditional method of preparation (a) and with preliminary plastic preparation and following granulation (b).

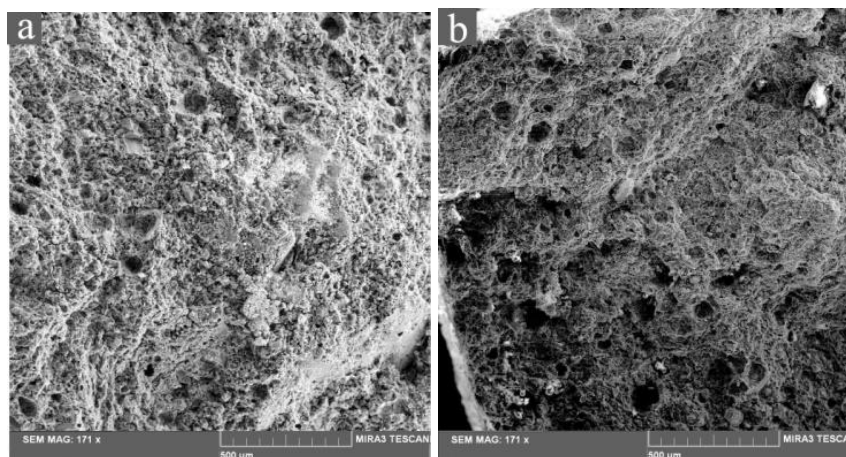
The phase composition of the burnt brick with calcium-containing additive was examined with diffractometer DRON-7. On figure 3 there are X-ray patterns of burnt at 1050°C samples, made from

pure clay raw material and with the injunction of 5% waste products. In both samples there are minerals – quartz, hematite and anorthite. In the sample containing mineral additive there is also a new crystal phase appearing – helenite ( $d/n = 2,85\text{\AA}$ ). The rising peaks in the X-ray pattern for ceramic brick with additive shows an increasing level of anorthite. The rise in crystal phases content is an increase cause of strength of samples containing the additive [16].



**Figure 3.** X-rays patterns of burnt samples with additive (a) and without additive (b)

The results of the analysis, carried out with the help of an electronic microscope, show that a modified brick contain a big amount pores in size of more that 100 mkm (figure 4).



**Figure 4.** Photographs of samples 170X magnification  
(a – pure raw material sample, b – a sample with additive)

The modifying additive effect on the porous properties, when examining the sample, was defined by the fact that due to the additive injunction volumes of total and opened porosity in burnt ceramic samples increased. The additive did not affect significantly on capillary and closed porosity. The amount of reserve porosity of burnt ceramic samples increased 2 times with using of waste products (table 3).



**Table 3.** Porosity characteristics of burnt samples

| Mass composition, %                          | Firing temperature, °C | Porosity, % |        |           |         |        |
|--|------------------------|-------------|--------|-----------|---------|--------|
|  |                        | Total       | Opened | Capillary | Reserve | Closed |
| Clay raw material – 100                      | 1050                   | 27.8        | 25.8   | 23.5      | 2.3     | 2.0    |
| Clay raw material – 95<br>Waste products – 5 | 1050                   | 31.3        | 29.2   | 24.3      | 4.9     | 2.1    |

The carried out researches demonstrate that the injunction of calcium-containing additive into clay mass with preliminary plastic preparation and following granulation leads to formation of optimal porous structure of ceramic brick and, consequently, to increase in frost resistance, influences the process of crystal formation with majority of anorthite and appearance of helenite, minerals which provide developing of strength properties of the material.

To evaluate the opportunity of practical appliance of received research results a test output of ceramic brick has been released by the factory OOO “Fili’N-KSM”.

The technological equipment of the factory (coarse grinding rolls, drying cylinder and disintegrator) did not enable to evenly process and homogenate ceramic batch mixture to reach necessary frost resistance characteristics, so the molding powder was produced in another conditions, separately, on experimental base. In the molding shop of the factory, from the given powder, with the help of a toggle-lever press there was produced an airbrick with 6% cavitation by means of two-stage two-side molding. Compression ratio was 1,8.

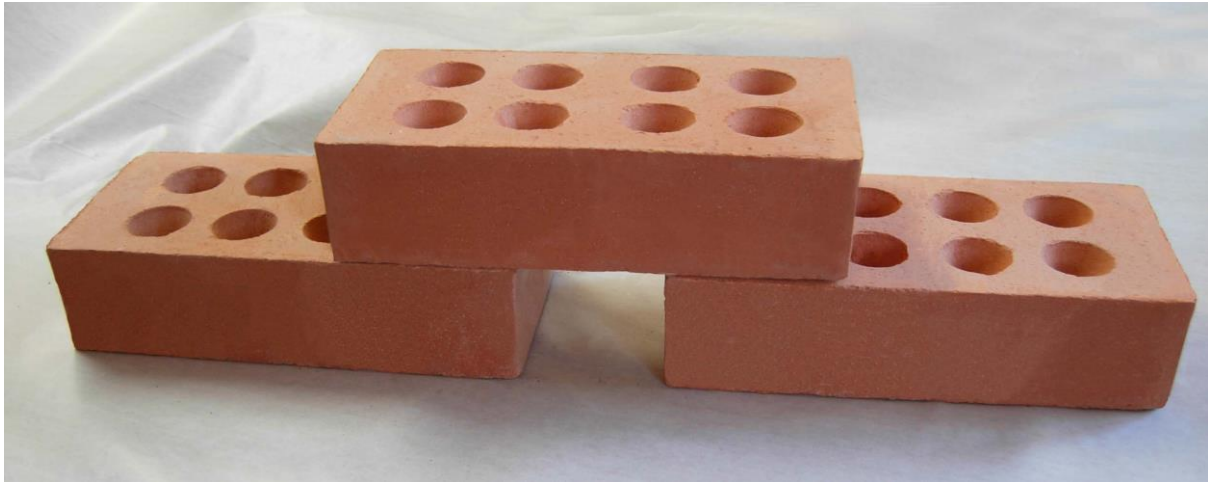
Firing of formed brick was carried out in a circular furnace of the factory with holding at maximum 1050°C. Burnt products satisfy GOST requirements according to their geometric dimensions and surface appearance. Performing of the tests of experimental brick has given the results presented in table 4.

**Table 4.** Results of physical-mechanical tests of experimental brick

| Name                             | Firing temperature, °C | Average density, kg/m <sup>3</sup> | Strength, MPa  |            | Water absorption, % | Frost resistance, cycles |
|----------------------------------|------------------------|------------------------------------|----------------|------------|---------------------|--------------------------|
|                                  |                        |                                    | On compression | On bending |                     |                          |
| Brick with waste products        | 1050                   | 1870                               | 16.4           | 2.8        | 13.7                | 52                       |
| Brick with fuel-bearing additive | 1050                   | 1828                               | 13.2           | 2.5        | 15.1                | 18                       |

Similarly to this, in the molding shop, there was one more lot of brick produced from the batch mixture made from the Atyukhtinsky field clay and fuel-bearing additive (factory-used composition). The results of the tests on basic strength and physical characteristics are presented in table 4.

The given ceramic brick containing waste products from fertilizers’ production, according to the surface appearance and frost resistance characteristics, is referred to lining brick (figure 5) in compliance with GOST 530, and on the surface there are no blooms and other defects caused by carbonate additives upon completion of tests.



**Figure 5.** Experimental brick with waste products additive

In such a manner, the use of the modified calcium-containing additive in the molding batch composition and thereby achieved characteristics of the received products confirm the fundamental possibility of producing lining frost resisting ceramic brick of semi dry molding, as is evidenced by the results of carried out researches and pilot-scale tests.

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