Use of Technogenic Additives in Facade Ceramic Tiles Production

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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.

1. Introduction
Refractory, infusible, less often low-melting clays that meet the requirements of GOST 9169-75 “Raw clay materials for the ceramic industry” Classification due to the ductility number, the content of large and medium ferrous minerals inclusions, gypsum and organic residues, high- or medium-sintering are recommended for the production of ceramic tiles. In Russia, the Ural (40%) and Central (18%) Federal districts with infusible clay of the Central (42%) one have significant reserves of developed refractory clays. Therefore, production capacities are concentrated mainly in the Russian European part and partially in the Urals (about 48%). The Siberian Federal District takes the second place in terms of refractory (26%) and infusible (33%) clays reserves. However, the share of developed deposits is very low (about 6%) [1], and the amount of ceramic tiles, produced by the Siberian region, is less than 0.1%.

The Novosibirsk Region territory has 3 deposits of infusible clays: Doroginskoye, Evsinskoye, Vassinskoye and Obskoye with refractory clays one. Fusible clay raw materials are represented by a large number of deposits, related to sediments of the Pachinskaya, Fedosovskaya, Krasnodubrovskaya, Chanovskaya and Karasukskaya suites. Significant part of these sedimentary rocks is represented by loams with low technological properties, as the studies of Tacki L.N. and other researchers of Novosibirsk State University of Architecture and Civil Engineering (Sibstrin) showed [2-4]. The high content of dusty particles causes an increase in sensitivity to drying and consequently susceptibility to cracking and low specimen raw materials. High content of carbonate inclusions increases the porosity of the ceramic crock and reduces its strength actions.

A promising raw material is natural and industrial wollastonite that acts as a micro-reinforcing additive. The research results of domestic and foreign authors [5-13] show that wollastonite
introduction in the composition of ceramic masses reduces the firing temperature and shrinkage of products. Wollastonite increases the brand of products and reduces their water absorption. Ceramic materials with the wollastonite addition are characterized by high resistance to cracking during firing and cooling. The mechanical strength of the products increases significantly.

Cullet can be considered as an additive providing a vitreous phase formation. Vitkalova I.A. and other authors [14] conducted a study of possibility of the most common cullet types using. They established the effect of additive amount and its chemical composition on the physicomechanical properties of ceramics.

The goal of this research work was to study the possibility of obtaining facade ceramic tiles, based on clay raw materials of the Novosibirsk region and mineral additives that meet regulatory requirements.

2. Materials and Methods

The basis of a charge was the clay raw material of the Bolotninsky and Evsinsky deposits for obtaining facade tiles. The clay raw materials of the Bolotninskoye deposit are low-melting mixture in terms of refractoriness and belong to dusty loam having the following chemical composition (in wt.%): SiO₂ – 61,00; Al₂O₃ – 12,54; Fe₂O₃ – 4,69; CaO – 5,67; MgO – 1,84 и R₂O – 4,70. The loam of the Bolotninskoye deposit belongs to the group of acidic by the content of alumina, and it belongs to the group with a high content of coloring oxides by the content of iron oxide.

The plasticity number is 10.9, in accordance with GOST 9169-75 “Clay raw materials for the ceramic industry. Classification”, allows referring to the group moderately plastic. Clays of the Evsinsky deposit were used as infusible ones, represented by the following chemical composition (in wt.%): SiO₂ – 63,70; Al₂O₃ – 15,57; Fe₂O₃ – 2,87; CaO – 3,19; MgO – 1,86 and R₂O – 3,60. The number of plasticity is 24, which classifies this raw material as a group of medium plastic ones.

Wollastonite grade VP-10 LLC Tekhnohim, Novosibirsk was used as a micro-reinforcing additive. Wollastonite is a calcium silicate, having the molecular formula CaSiO₃. This is a fine powder of white color (whiteness - 96.0), which main fraction has a size of 75 microns. Wollastonite has a pH = 9.8, which allows it to be alkaline. The melting point of wollastonite is 1540 °C.

Cullet glass of (CC-1 grade), GOST R 52022-2003 “Glass containers for food and perfumery -cosmetic products. Glass brands” was used as additives to ensure the formation of the vitreous phase.

The chemical composition of the additives is given in table. 1.

| Additive   | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | MnO | R₂O | P | H₂O |
|------------|------|-------|-------|-----|-----|-----|-----|---|-----|
| Wollastonite | 50.89 | 0.19  | 0.33  | 44.76 | 1.55 | 0.044 | -  | 0.03 | 0.12 | 2.1 |
| Cullet     | 71.40 | 1.80  | 1.20  | 9.90  | 2.60 | -    | 13.60 | -  | -   |

Pre-dried raw materials clay and cullet were crushed in a ball mill until they passed through a sieve No. 0.63 during testing.

The suitability of raw materials clay for obtaining facade tiles and their quantitative ratio was determined by the classification diagram of clay according to A.I. Augustiniku and V.F. Pavlov [15]. The initial chemical composition of raw materials clay was recalculated according their mixture parameters, taken as the low-melting ratio - 60%, refractory - 40% in order to use the diagram. The resulting chemical composition of the raw materials clay’s mixture was reduced to 100% per calcined substance, and then converted into mol (table. 2).

The diagram is based on molar ratios, where the ratio of alumina to silicon oxide is deposited along the “y” axis, and the moles sum of calcium, magnesium, sodium, potassium and iron oxides is deposited along the x-axis. The intersection point of straight lines, lowered from the axes, indicates the area corresponding to the clay in order to obtain a certain type of ceramic tile.
Table 2. Determining the suitability of raw materials clay for facade tiles.

| Initial data          | The content of oxides, wt.% | Σ     |
|-----------------------|----------------------------|-------|
|                       | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | R₂O  | P.p.p. |       |
| Bolotninskoe (out),   | 61.00| 12.54 | 4.69  | 5.67 | 1.84 | 4.70 | 7.42   | 97.86 |
| Evsinsky (out)        | 63.70| 15.57 | 2.87  | 3.19 | 1.86 | 3.60 | 7.85   | 98.64 |
| Clay mixture 60:40    | 62.08| 13.752| 4.374 | 5.164| 2.04 | 4.703| 7.592  | 90.58 |
| 100% recount          | 68.536| 15.182| 4.374 | 5.164| 2.04 | 4.703| -      | 100   |

The content of oxides, mol

|           | 1.14 | 0.1489 | 0.027 | 0.92 | 0.05 | 0.03 | -      | -     |

Figure 1. Classification of clay according to A.I. Augustinique (1-3) and V.F. Pavlov (I-III) [15]: 1- clay, suitable for the refractories production; 2- the same for acidproof, sewer pipes, stone goods; 3- the same for building bricks; 1 - in the tiles’ manufacture for floors and facade; II- facade and facing tiles; III- facing tiles.

The diagram (Figure 1) shows the calculated composition of raw materials clay falls into zone II, which corresponds to the facade tile. Therefore, the mixture of low-melting and refractory raw materials clay of 60:40 ratios is taken as the main one.

Charge composition of the mixture was optimized by mineral additives using the multifactorial design method of the experiment to obtain response functions and nomograms that connect parameters output (y₁ is the compressive strength, MPa; y₂ is the amount of water absorption,%) with variable factors (x₁ is cullet content,%; x₂ is wollastonite content,%), varying within the range: x₁ from 0 to 10%, x₂ - from 0 to 15%. 4 types of mixture were prepared for the facade tile according to the experimental plan, which included the required amount of additive, taken by weight of raw materials clay:

- 1 composition was 10% glass and 15% wollastonite;
- 2 composition was 15% wollastonite;
- 3 composition was 10% cullet;
- 4 composition was a mixture of clay raw materials (control).

Cylinders samples of 40 mm in diameter were formed from each charge by the method of semi-dry pressing. The moisture content of the press powder was 12%. The two-stage pressing mode with one-
sided application of load, with holding at a maximum pressure of 20 MPa was for 30 seconds. Pressing was carried out on a hydraulic press with a capacity of 100 kN. The obtained cylinder samples were first dried as follows: two days under a damp cloth, and then dried to constant weight in an oven at a temperature of 100 - 105 °C. Firing was carried out in a laboratory muffle furnace at a temperature of 1150 °C. The temperature rise was 200 °C per hour. The isothermal exposure was 1 hour. The samples were cooled naturally in the furnace. Figure 2 shows photographs of dried and calcined samples.

Figure 3. Photographs of samples: a is dried at 105 °C; b is calcined at 1150 °C.

The physicomechanical properties of the dried and calcined samples were evaluated by standard methods for ceramic materials.

3. Results
Air and fire shrinkages, average density, water absorption, ultimate compressive strength, and softening coefficient were determined for each composition. The test results are presented in table 3.
Table 3. Physico-mechanical properties of samples.

| Composition number | Shrink% | Average density, g / sm³ | Water absorption, % | The limit of compressive strength, MPa | Softening coefficient |
|--------------------|---------|--------------------------|--------------------|----------------------------------------|----------------------|
|                    | Aerial  | Flamed                   |                    |                                        |                      |
| 1 composition      | 0.025   | 4.890                    | 2.058              | 0.91                                   | 85.85                | 0.98                |
| 2 composition      | 0.0625  | 6.702                    | 2.162              | 1.62                                   | 87.50                | 1.00                |
| 3 composition      | 0.0875  | 2.237                    | 1.83               | 7.4                                    | 77.94                | 0.86                |
| 4 composition      | 0.2     | 2.262                    | 1.79               | 10.14                                  | 69.90                | 0.96                |
| (control)          |         |                          |                    |                                        |                      |

The research results (Table 3) showed that, it was possible to obtain a ceramic crock with a density of 1.79 g / sm³ and water absorption of 10%, taken in a ratio of 60:40 and calcined at a temperature of 1150 °C from a mixture of low-melting and refractory clays which met the requirements of GOST 13996-93 “Ceramic facade tiles and their carpets. Technical conditions” for polymineral clays of not more than 12%.

10% amount of cullet introduction in the control composition reduces the air shrinkage of the samples by 2.27 times, which allows us to consider cullet as an exhaustive additive at the stage of raw production. Flamed shrinkage of this charge composition varies slightly. During firing, the presence of cullet in the charge composition leads to the formation of a glassy phase, filling the pores in the material bulk, thereby contributing to an increase in the average density of the ceramic crock and an increase in compressive strength by 10.3% and a decrease in water absorption by 27%.

A further decrease in air shrinkage of composition samples No. 2 is associated with an increase in the amount of introduced mineral additives by 5%. In this case wollastonite manifests itself as a depleting additive, determining pre-calcining properties. An increase in flamed shrinkage to 6.7% is explained by the fact that it begins to show a fluxing effect, increasing volume of liquid phase and denser sintering of the samples at a firing temperature above 1100 °C in the process of wollastonite introduction into the charge. The resulting liquid phase fills more pores, increasing the average density of the ceramic crock by 17.2%, compared with the control composition. An increase in the mechanical strength of composition samples № 2 by 10.9% is associated with the creation of a more dense ceramic shard structure and the effect of reinforcement with wollastonite crystals in comparison with composition № 3. The creation of a dense structure helps to reduce water absorption to 1.62%.

4. Conclusion

Ceramic crock strength begins to decrease, since the layers thickness of vitreous phase increases so much that its fragility and lower strength compared to the crystalline phases begin to affect strength characteristics of the samples with the combined introduction of glass and wollastonite. Intensity decrease in water absorption of this composition is explained by the fact that, only the pores are the unfilled glassy phase, where the melt can not penetrate due to insufficiently low viscosity in the process of wollastonite and cullet co-introducing; therefore, the decrease in water absorption occurs only due to an increase in the glassy phase proportion in the volume of material.

Thus, the study showed that it was possible to produce facade tiles that met the requirements of GOST 13996-93 “Ceramic facade tiles and their carpets from the low-melting clay mixture of the Bolotninskoye field and refractory clay of the Evsinskoye field. Technical conditions”, and the introduction of directional mineral additives helped to improve its physical and mechanical properties.


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