INDUSTRIAL OBTAINING BRICKS COVERED WITH ZEOLITE-BASED GLAZING

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INTRODUCTION

Glazed bricks are among the most attractive finishing materials as apart from the decorative looks they have a rather high strength and resistance against aggressive media, and do not let water and microorganisms through. A big list of their merits allows applying them not only as a façade material, but also for laying interior walls in rooms and simply for the decorating the interiors and exteriors of buildings.

However, obtaining glazed bricks is associated with some complications, for example, the procurement of new equipment, commissioning of additional production line, purchase of expensive raw materials. Zeolite application for the glaze production as the basic raw material will help solve a number of difficulties due to multiple zeolite natural deposits and its ability to glass formation.

According to previously obtained data, we have discovered that zeolite is a promising raw material for obtaining glazes on ceramic objects. We have proved experimentally that a batch to melt at 1000°C and to form crystal-glass coating on the surface of a ceramic object can be obtained by mixing flour zeolite with various additives. Due to the experimental studies, in laboratory conditions we obtained samples of crystal-glass glaze on ceramic crocks (Pozhidaev, et al., 2016). Glaze application to ceramics allowed us to conceal the surface defects, add lustre to it and change the colour. Such results suggest that by using this technology one can obtain glazed bricks since the...
temperature of the glaze obtaining is close to the brick firing temperature. To prove this supposition, we performed an experimental study in the laboratory and at the ceramic brick manufacture factory located in the Primorsky Kray, Russian Federation, in the city of Nakhodka (township Wrangel), owned by the Limited Liability Company "Zavod Stroitelnoy Keramiki".

During the experiments, the first series were fired with "wet" method, then the samples were transmitted for X-ray analysis. After the X-ray-phase analysis results were studied, we decided to kiln the fritted glaze.

As a result, we managed to get a glazed brick covered with crystal-glass glaze at two sides, which after that was tested for freeze-thaw resistance.

**EXPERIMENTAL METHODS**

On the whole, 25 compositions were developed, which were split into 3 experimental series. The process of the batch production included three phases.

Phase one-preparation of the raw material. All batch components, non-water-soluble, were grinded in a flint mill, and screened through a mesh screen with 0.16 mm cells with the residue of under 5%. Phase two-all components were weighed on electronic scales with the scale division of 0.01 g. Phase three-mixing the components. First, all water-soluble components were mixed, then water was added to the mixture to get the required concentration. After water was added, the composition was thoroughly mixed until all components are dissolved in water and form a homogeneous fluid. Then non-water-soluble components were added to the mixture and the composition underwent the final mixing. All compositions were mixed in polypropylene vessels (Pozhidaev and Gulyaev, 2016).

Zeolite is the base of the compositions, as it imbibes water very well and adsors various chemical elements; therefore, the obtained batch compositions could be distinguished by a high grade of homogeneity and did not unscramble. Such batch samples consolidated with the surfaces of ceramic objects very well, where they had been applied with a polypropylene palette knife. Low-melt components, such as sodium hydroxide, potassium hydroxide and sodium tetraborate, were introduced in the batch composition in the doses from 5% to 25%, and other components, e.g., chrome oxide or magnesium oxide, were introduced in the concentrations from 2 to 3%. To secure better mixing and reaction progress, a super plasticizing admix based on the plasticizer C3 was introduced in the composition (Zhernovaya, et al., 2013).

The chemical composition of the zeolite produced at the Chuguevsky natural deposit was studied before and presented in the article about obtaining glazed coatings on ceramic items (Pozhidaev, et al., 2016).

After that, all prepared samples were put on a special industrial conveyor to feed the samples to the kiln. The tunnel-type kiln is conditionally split into 7 areas, in each of which certain temperature is maintained. In the central 4th area, the oil residue is burnt to heat the kiln up to 980°C. The gases produced by the burning oil residue propagate from the 4th area to other areas of the kiln; thus, in the 1st and the 7th areas the temperature is 100°C, in the 2nd and the 6th areas the temperature is 400°C, and in the 3rd and in the 5th areas the temperature is 700°C. While moving through the kiln, the bricks were gradually heated and then gradually cooled. On the average, the kiln process took from two to four days as the line was not loaded to the full, the bricks had to stay in the furnace for quite a long time, so the process took 4 days.

The batch compositions fired in the laboratory conditions were prepared basing on the same principle, but fired in the muffle furnace, where the temperature rise and falls were regulated with a thermoregulator. The firing process took 44 hours, out of which 22 hours were spent on heating and 22-on cooling; this was enough to fire clay into ceramics, and to melt the batch into glaze and, thus, obtain a sample with the ambient temperature (Aurélio, et al., 2015).

The first experimental series included 12 compositions and were fired at Zavod Stroitelnoy Keramiki, LLC. The second experimental series included six pairs of compositions (12 samples on the whole) with pair-wise identical compositions. In the result, six compositions were fired in the muffle, and other six-at the factory in the tunnel-type kiln. The third, the last, experimental series included the composition that had previously shown itself as the best one. That composition was prepared in the laboratory and first fired in the muffle furnace, after which the obtained glaze was grinded in the flint mill and applied to an air-dried brick, that was then fired in the tunnel-type kiln at the factory and after that tested for freeze-thaw resistance.

**STUDY RESULTS AND PROCEDURE OF WORK**

Fist experimental series. Compositions were
prepared and applied to the surfaces with the above-described method. On the whole, 12 batch samples were prepared; their compositions are shown in Table 1.

The compositions were developed basing on the previously performed experiments, but with higher concentrations of low-melt components, as well as of additionally introduced other components to trace their response at the firing in the industrial furnace. The batch compositions were applied to the fragments of air-dried clay using a polypropylene palette knife (Anufrik, et al., 2016; Partyka and Lesniak, 2016).

As a result of the firing, the batch did not gain the amorphous structure, and no glaze was formed.

The second experimental series included 12 compositions presented in Table 2.

The compositions were selected so that to allow the analysis of the effect of a large spectrum of components on the main glaze properties; therefore, we can see eggshell here as the source of calcium, and cooking salt as the source of chlorine. Eggshell is non-water-soluble; therefore, it was grinded and mixed with zeolite separately from other components.

As we can see in Table 2, the compositions are duplicated, and there are six pairs of compositions. Thus, the samples with identical methods of preparation and compositions were fired in different conditions: with uneven numbers-in laboratory conditions, with even numbers-in factory conditions in the industrial kiln. In this way, we can trace the effect of the firing environment on the result.

After firing, the samples with uneven numbers were melted to the glaze, while those with even numbers were not; therefore, the fragments of the compositions were transmitted to the laboratory for the X-ray phase analysis. This is required to determine the main differences in the compositions of the coats and to determine what had produced such effect on the firing results. The graphs obtained after the X-ray phase analysis are shown in Fig. 1 and 2.

**Table 1. Compositions in the first experimental series**

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<th>S. No.</th>
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<th>ZnO</th>
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**Table 2. Compositions in the second experimental series**

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Fig. 1 shows the X-ray phase analysis curves for the samples No.1, 3, 9, 11. We can see that the samples fired in the muffle furnace have changed their structure after firing and became amorphous, as their curves do not have spikes characteristic for any separate conglomerate. At the same time, Fig. 2 shows spikes; the circled spike suggests the presence of calcium sulphate, the melting temperature of which is 1460°C, which is significantly higher than the planned firing temperature.

This is due to the zeolite properties, namely its ability to absorb sulphur oxides that get into the composition with the smoke emitted by the oil residue at combustion. But if we use the already fired amorphous glaze for glazing the surface of an item, we can avoid the effect of the oil residue combustion products (Leśniak, et al., 2016).

The objective of the third experimental series was to obtain glazed bricks. Taking into account the previously analyzed results, we decided to frit the glaze prior to industrial firing. Thus, we prepared and fired in the muffle furnace 150 g of glaze with the following composition:

- Zeolite-52%;
- NaOH-10%;
- KOH-10%;
- Na₂B₄O₇-5%;
- Plasticizer-3%;
Fritted glaze was grinded in a flint mill and screened through a mesh screen with 0.16 mm cells with the residue of under 5%. After that, the glaze was mixed with the PVA adhesive under the 4:1 ratio and applied to the air-dried brick. Such brick was sent for firing in the industrial kiln. As a result, we had a brick, the two faces of which (header and stretcher) were covered with the dark-green glass-like glaze with contoured surface. The freeze-thaw resistance tests showed that the brick met the F50 freeze-thaw resistance grade (Partyka, et al., 2016).

**DISCUSSION OF THE STUDY RESULTS**

After the firing of the first experimental series, the glaze did not form and no glass-like substance was on the ceramic surface; all batch compositions did not melt or partially melted on the surface. The samples of the compositions fragment-wise spread on the ceramic surface without forming a uniform structure.

The second experimental series was performed to

![Fig. 3 Results of the second series industrial firing.](image1)

![Fig. 4 Results of the second series laboratory-based firing.](image2)
determine the reasons for such results; the outcome of the second series is shown in Fig. 3 and 4.

The pictures suggest that the batch compositions with uneven numbers were well burnt and melted completely, and after cooling got the glasslike condition, except No. 2.7 and 2.11, which had passed to the amorphous condition on the surface only. The compositions No. 2.3 and 2.9 gained white colour, which, most probably, was caused by the presence of chlorine in the batch, but still they had quite high surface tension force that does not allow the glaze to spread. At the same time, all the compositions fired at the factory did not spread and did not become amorphous. To check the supposition about the oil residue combustion product effect on the firing results, the fragments of the coating were transmitted to the laboratory for the X-ray phase analysis (Castela, et al., 2010; Zhu, et al., 2015).

The X-ray phase analysis indicated that the sulphur oxide emitted at the oil residue combustion was absorbed by zeolite and changed the batch composition. In the course of heating, when the connections between various batch components are being broken, the sulphur oxide enters into reaction with calcium (from zeolite) with generating calcium sulphate, which increases the batch melting temperature and prevents the glaze from forming.

Preliminary cracked samples of glaze obtained in laboratory conditions were sent into the kiln to check that hypothesis. After firing, the cracks disappeared, which indicate that the glaze melted in the kiln, but did not collapse. Thus, we discovered that the oil residue combustion products did not affect the already fired glaze; hence, we could obtain the glazed brick using fritted glaze (Tunali, et al., 2015).

Fig. 5 shows one sample of glazed brick obtained in the third experimental series.

On the whole, we obtained 3 items of glazed bricks after firing the third experimental series at the factory. As they have been only the first experimental prototypes, it would be unwise to deem that 150 g of fritted glaze were spent for obtaining the glazed bricks. This is due to the fact that the process of glaze application on the air-dried brick is not worked out completely—some portions of glaze get lost at transportation, application and firing.

The obtained glaze evenly covered the surface of the brick where it had been applied to, did not have drips, and firmly attached to the ceramic surface. The glaze, in its depth, had a number of closed interconnected pores due to which it gained scalloped surface. The colour of the glaze was dark-green, and visually changed to black depending on the distance and the angle of observation. The glaze was rather hard and it was practically impossible to make scratches with a riffler on it, which can be characterized by the hardness of 5-6 on the Mohs hardness scale (Ghosh, et al., 2013).

The samples obtained after the third experimental series were transmitted to the laboratory of Zavod

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**Fig. 5** Results of the third series firing.
Stroitelnoy Keramiki, LLC, where they were tested for freeze-thaw resistance using the method of alternating freezing and thawing. The obtained results proved that after fifty cycles of alternating freezing and thawing the glaze did not collapse, no cracks were formed, it did not break loose and peel off; hence, the coefficients of thermal expansion of the glaze and ceramics matched each other, and the glaze freezing and thawing resistance can be characterized by at least grade F50.

CONCLUSION

The main results of the conducted study are as follows:

- Zeolite is a promising raw material for obtaining glazes and glasses at the softening point below 1000°C.
- We obtained a zeolite-based glaze, the melting temperature of which was identical to the brick firing temperature. That glaze is resistant against industrial firing conditions.
- Adding chlorine to the batch composition allows gaining white colour for the glaze immediately after firing.
- In the ceramic brick production factory conditions, we obtained dark-green glazed bricks.
- The coefficients of the ceramic crock and glaze thermal expansion match each other which is testified by the freezing-and-thawing resistance test results.
- When the firing in the kiln is performed due to the oil residue combustion, and the combustion products go through the firing chamber along with the smoke, the zeolite-based glaze cannot be obtained. In such cases, the glaze must be fritted; then the zeolite structure changes and it stops absorbing sulphur.

In further studies, we plan to obtain white as well as transparent glaze. Later, the production process of glaze application and firing glazed items will be developed to allow making the glazed brick production convenient, scalable and inexpensive (Sheikhattar, et al., 2016; Kalirajan, et al., 2016).

REFERENCES