

The influence of coloring admixtures on zeolite-containing glazes

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Abstract

The research was carried out within the framework of zeolite-containing glazes' development based on the previously obtained results. This paper was devoted to obtaining low-melting (1,000°C) silicon-sodium colored glazes. Compositions of the glazes were developed in order to make them white, green and purple. The main part of the tested compositions was zeolite, to which wollastonite was added. Oxides of chromium (II), manganese, zinc and magnesium were used as self-coloring pigments. To lower the melting and vitrification temperature, the following fluxes were used: sodium hydroxide, sodium tetraborate and potassium hydroxide. The total of 24 compositions were developed and tested, which were burned at the maximum temperature of 970°C in a muffle furnace, 12 compositions in one series of the experiment. After the tests, green, black, violet and white glaze samples were obtained, and the influence of component composition on the color and the characteristics of the glaze during melting and cooling were determined. It was possible to observe the process of glaze devitrification to its complete crystallization, and to determine the parameters, compliance with which would allow avoiding devitrification of zeolite-containing glazes. Some compositions had no signs of melting after burning, which allowed to determine the influence of the component composition on the melting point of the furnace charge.

Keywords: zeolite, wollastonite, glaze, batch, glaze color, glaze devitrification.

INTRODUCTION

In the previous works, it became possible to obtain glazes of various colors by using zeolite-containing rocks. With the addition of sodium, chloride, wollastonite and potassium to the glaze, it was possible to obtain black, white, green and white-green colors with glossy and matte surfaces. This was due to the fact that concentration of these minerals in the furnace charge caused the reaction of glaze coloring by pigments substances in the composition of zeolite, but incapable of staining; otherwise, staining was achieved due to self-pigmenting substances, such as chlorine that was supposed to evaporate but remained in the composition due to zeolite, and gave the uneven white color to the melt. [1]

This paper was aimed at studying the influence of pigments substances capable of independent coloring on zeolite-containing glazes. Chromium, manganese, zinc and magnesium were used as self-coloring elements. This work was aimed at obtaining green, purple and white glossy and matte glazes. It was assumed that weak concentration of colorants would not increase the melting temperature; however, various concentrations were used for determining the dependence of melting intensity on the concentration of certain colorants. [2]

The glazes obtained might be attributed to the silicon-and-sodium ones, since their compositions were dominated by these two elements. The main share of furnace charge was zeolite - the rock obtained from deposits by underground or above-ground method, in the form of gray stones with the fraction size of 10-40 mm. For obtaining glazes, it should be milled to fraction size 0.08 mm, which was made by crushing large rocks in a roll-jaw crusher, followed by milling in a ball mill for 6-8 hours. Sodium hydroxide, potassium hydroxide and sodium tetraborate (hereinafter referred to borax) were added to zeolite as fluxes. To make the glaze transparent, wollastonite obtained synthetically was added to the furnace charge, and for better mixing in small amounts of water and for adding silica fume, plasticizer based on plasticizer C3 was introduced into the furnace charge. After that, pigments additives were added to the furnace charge. [3]

METHODS

After adding all the components, the furnace charge was mixed in a mechanical paddle mixer during 20-25 seconds, and placed into a polypropylene container, to which the required amount of water was added. After mixing with water, the resulting homogeneous viscous mass was applied to the samples of dried clay, and they were sent to the furnace. A front-loaded muffle furnace was used; the calcination temperature was adjusted using a thermostat that allowed monitoring heating and cooling rate, as well as exposure to preset temperatures with the accuracy of a minute or a degree Celsius.

The maximum samples' burning temperature was 970 °C, they were gradually heated with exposure to 80, 100, 400, 700 and 970 °C. Upon completion of the burning process, the furnace was automatically switched off and cooled down; the samples were removed when the temperature in the furnace dropped to 50 °C. [4]

During the research, two series of experiments were made, where 12 compounds of the furnace charge were tested. The total of 24 compositions of furnace charge was tested this way; their component compositions are shown in Table 1.

This component composition was developed with the aim to determine the influence of oxides of chromium, manganese, magnesium, and zinc on the furnace charge with various shares of zeolite/wollastonite/sodium hydroxide.

In the previously made experiments, when oxides of manganese and chromium (2% by mass) were added into the zeolite-containing glazes without wollastonite, samples covered with black and green pigment layers were obtained. This phenomenon was due to these oxides' distribution across the surface of the melt. Then mixing was performed manually; now, with the introduction of mechanical mixing and decreasing the content of these oxides, it was decided to test their effect on the glaze, without formation of the surface films. [5]

Zinc and magnesium were often used in glazes as whiteners, which allowed achieving white color of the glaze. To determine the optimum concentrations of the admixture, 1 to 5% were introduced, and their joint effect was also studied.

By visual inspection, the samples were checked for the presence of cracks, delaminations, signs of melting, color, and transparency. Then hardness of the surface layer was tested by the Mohs' scale.

Table 1. Furnace charge component compositions (developed by the author)

No.	Content in % / g										
	Zeolite	Wollastonite	NaOH	Borax	C3	Water	ZnO	KOH	MnO	MrO	ZrO(II)
<i>First series of experiments</i>											
1.1	38	8	10	10	3	20	-	10	-	-	1
1.2	38	8	10	10	3	20	-	10	-	1	-
1.3	38	8	10	10	3	20	1	10	-	-	-
1.4	36	8	10	10	3	20	3	10	-	-	-
1.5	34	8	10	10	3	20	5	10	-	-	-
1.6	38	8	10	10	3	20	-	10	1	-	-
1.7	36	8	10	10	3	20	-	10	3	-	-
1.8	34	8	10	10	3	20	-	10	5	-	-
1.9	32	5	15	10	3	20	5	10	-	-	-
1.10	32	5	15	10	3	20	-	10	5	-	-
1.11	33	8	10	10	3	20	3	10	3	-	-
1.12	31	5	15	10	3	20	3	10	3	-	-
<i>Second series of experiments</i>											
2.1	41	5	10	10	3	20	-	10	-	-	1
2.2	41	5	10	10	3	20	-	10	-	1	-
2.3	41	5	10	10	3	20	1	10	-	-	-
2.4	39	5	10	10	3	20	3	10	-	-	-
2.5	37	5	10	10	3	20	5	10	-	-	-
2.6	41	5	10	10	3	20	-	10	1	-	-
2.7	39	5	10	10	3	20	-	10	3	-	-
2.8	37	5	10	10	3	20	-	10	5	-	-
2.9	29	8	15	10	3	20	5	10	-	-	-
2.10	29	8	15	10	3	20	-	10	5	-	-
2.11	36	5	10	10	3	20	3	10	3	-	-
2.12	28	8	15	10	3	20	3	10	3	-	-

RESULTS

As a result of the burning in the first series of experiments, it was found that some formulations of the furnace charge melted to the state of glass, while other samples retained crystalline structure. It should also be noted that on the surfaces that retained their crystalline structure, traces of melting were observed – the layer of furnace charge was uniformly distributed on the surface, but the pores that indicated softening of the furnace charge with the release of gases were observed. Figure 1 shows the results of burning the first series of experiment.

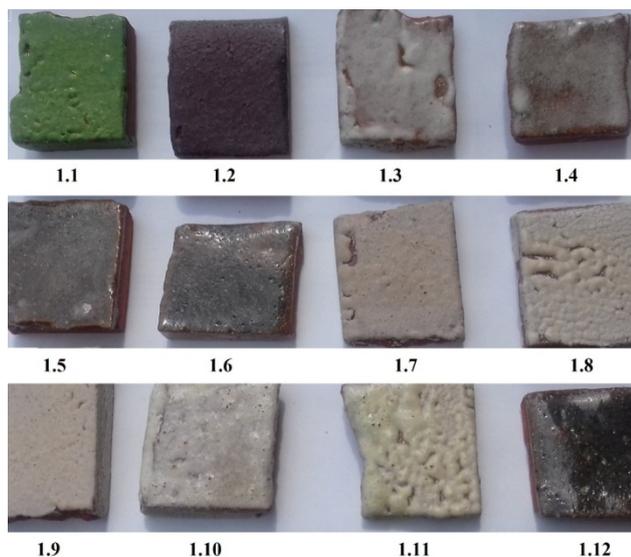


Figure 1. The results of burning the first series of experiments (developed by the author)

The image shows that only compositions No. 1.4, 1.5, 1.6 and 1.12 formed the glassy coating. Compositions No. 1.1 and 1.2 were firmly fixed with the uniform matte layer, in which pores occasionally stood out; the color of the coatings was dull, sample No. 1.1 was green, and No. 1.2 was violet. Compositions No. 1.3, 1.4, 1.7, 1.8, 1.9, 1.10, 1.11 were of dull matte milky color, and No. 1.5, 1.6, 1.12 were of translucent dark green color. Compositions No. 1.3 и 1.10 melted down, the gloss indicated the presence of the vitreous mass, but its content was insufficient. On the rest of surfaces, there were traces of melting; the changes of the volume were especially visible in coatings of samples No. 1.8 and 1.11, in which the entire surface was covered with closed pores. According to the results, it could be assumed that during burning, the furnace charge melted, but when cooled, certain compositions partially or fully crystallized. [6]

It should be noted that on the surfaces of samples No. 1.5, 1.6 and 1.12 devitrification was observed, and the surface was covered with open pores, which gave them the matte finish. The surfaces of samples No. 1.3 и 1.4 were also matte, but here it was due to the dull color of the milk-colored glaze. Otherwise, it should be noted that compositions No. 1.9 and 1.7 were uniformly distributed on the surface, and had almost no pores; possibly, these compounds were not melted. The samples' hardness by the Mohs' scale had been determined equal to 6. [7]

In the second series of experiments, particles of wollastonite were replaced by zeolite, since the previous works had shown that the increased concentration of wollastonite had resulted in devitrification (crystallization) of glaze. However, at high concentrations of sodium, it was decided to increase the concentration of wollastonite for doubling the compositions from the first series of experiments. By the results of burning, samples shown in Fig. 2 were obtained.

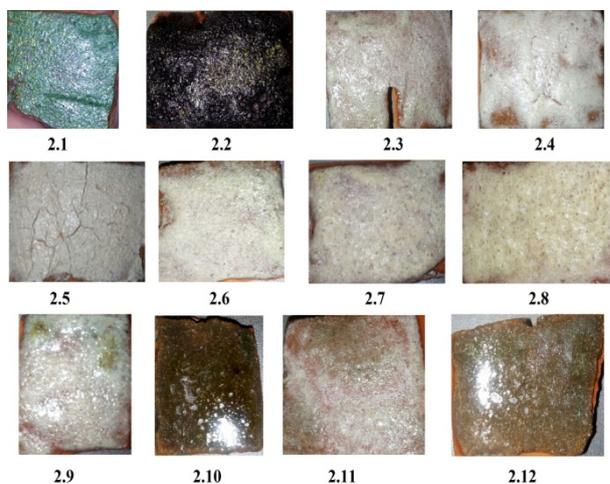


Figure 2. The results of burning the second series of experiments (developed by the author)

Comparison of the samples of the first and the second series showed considerable differences. Samples No. 2.1 and 2.2 were shiny, and the entire surface was covered by opened pores; the color of coating No.1.1 was green and that of No. 2.2 was black with violet tint. The surfaces of samples from No. 2.3 to 2.9 and No. 2.11 were rough, of matte milky color; surfaces of No. 2.3, 2.4, 2.9 had weak scattered glitter. Composition No. 2.5 was cracked, and the surfaces of No. 2.6 – 2.9 and 2.11 were covered with pores. The glossy glitter was only seen in samples No. 2.10 and 2.12, translucent dark green coatings with foci of devitrification on the surface. The samples' hardness by the Mohs' scale was determined equal to 6. [8]

DISCUSSION

Since compositions No. 1.1 and 2.1 after melting were completely colored green, it could be stated that chromium concentration of 1% by weight of the glaze was sufficient for complete coloring. Surfaces No. 1.2 and 2.2 were colored, if engobe of violet color was obtained instead of glaze, then manganese concentration of 1% was sufficient for coloring; if glaze was required, manganese concentration should be reduced, same as that of wollastonite.

Zinc and magnesium colored the glaze white, but the introduction of magnesium, unlike zinc, led to significant devitrification, glazes with zinc had soft diffused glitter and pleasant texture, unlike the coarse granular texture of magnesium glazes. Glaze devitrification might be avoided by increasing the concentration of sodium in the furnace charge, but it might affect the properties of the glaze. [9]

Substitution of some wollastonite in the composition of the furnace charge with zeolite made zinc glazes more heat-proof; thus, sample No. 2.5 got covered with cracks, but no traces of melting had been found. Substitution of some wollastonite with zeolite in magnesium glazes, on the contrary, allowed the glazes to melt at 970°C, but the viscosity of the melt did not let all gases leave the body of the glaze, and craters were formed on the surface, while the melt crystallized during cooling. Increasing the concentration of sodium in the compositions of glazes with magnesium and zinc led to melt hardening in the form of glass, but the process of devitrification was still observed.

CONCLUSION

Analyzing the results of the first and second series of experiments, it could be stated that the introduction of chromium and manganese oxides into zeolite-containing glaze increased the melting temperature together with wollastonite, while decreased concentration of wollastonite increased the intensity of glaze melting at the same temperature.

Zeolite-containing glazes with the addition of magnesium, on the contrary, melt more intensively as the temperature decreased, but the quality of the surface layer did not let consider it decorative. [10]

Chrome colored the zeolite-containing glazes green, regardless of its structure and state; at the same time, manganese colored not-crystalline engobes violet, and vitreous glaze – black, when manganese oxide concentration was 1%.

High concentrations of wollastonite, zinc and magnesium led to glazed devitrification, or its crystallization from

the melt during cooling; this might be avoided by replacing part of zeolite with sodium, but this might degrade glaze quality.

Making glaze white required the introduction of 1 to 3% of zinc oxide (with sodium hydroxide and potassium concentration of 10%) into the composition of the furnace charge; exceeding this concentration resulted in devitrification of the glaze during cooling.

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