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Use of local raw materials to obtain glass used in glazing of ceramic products

Abstract. Glass is one of the widely used materials in the construction industry and in everyday life. The year-on-year growing demand for various types of glass products pushes the glass-making industries to increase their production volumes and not to lower their quality levels. The scientific and technical progress in glass extraction has gradually expanded the area of its effective use. In recent years, significant changes have taken place in the glassmaking technique. New production methods and ways of improving existing technological processes appeared, and new areas of glass application began to open. The chemical composition of the product was changed, and different types of glass were made. In this regard, the study of the method of obtaining glass with different properties is one of the most important issues. In order to prepare the composition of colored glass used in the production of various products, colored glass was obtained in laboratory conditions. Physico-chemical properties of the obtained colored glass were studied in order to determine the area of application. Based on the research results, the obtained colored glass can be used for decorative purposes.
Key words: colored glass, glass charge, sand, soda, slaked lime, thermal stability, chemical stability.

Introduction

Glass is an amorphous material obtained by cooling the melt. Raw materials used in glass production are conditionally divided into basic and auxiliary. Main raw materials for glass production: quartz sand, soda, dolomite, feldspar, calcium carbonate, etc.; and auxiliary raw materials include bright color givers, decolorizers, dyes, quenchers, oxidizers (carbon substances) [1-3].

Quartz sand is the main material used in the introduction of silica into the composition of glass. Silica SiO_2 is the main component of silicate glass. The main requirement for sand is to have a large amount of SiO_2 in it, and a very small number of impurities (including iron oxides). The silica content of the sand used in glass baking should not be less than 95%. In addition, the sand contains additives that change the color of the glass mass during the glass baking process. Such additives include iron oxide, titanium, vanadium, chromium oxides. The amount of these additives should be very small. Pure quartz glass is obtained from quartz sand. It requires a temperature of 1850-1950 ºC. That is, the melting temperature of sand is very high and requires a long time [4-7].

That's why other additives are added in order to reduce the melting point of sand in glass production [8]. It includes naturally occurring chalk, marble, feldspar, etc. In addition to minerals, synthetic additives can also be used. These additives give different properties to the glass.

The presence of alkali metal oxides (Na_2O, K_2O) in the glass reduces its thermal and chemical stability, reduces its mechanical and dielectric properties. It also reduces melt viscosity and glass baking temperature. The amount of alkali metal oxides in the glass does not exceed 14-15%. Sodium oxide is introduced using soda ash and sodium sulfate, and potassium oxide is introduced using potash and saltpeter. Calcined soda is the main material used in the introduction of sodium oxide into glass. A white powder that dissolves well in water. During the glass baking process, soda decomposes into sodium oxide and carbon dioxide. Sodium sulfate Na_2SO_4 is difficult to decompose during glass baking. That is why carbon reducers (coal, sawdust) are added to the charge. The purpose of adding sodium sulfate to the charge is not to replace soda ash, but to facilitate the glass baking process. Potash K_2CO_3 consists of 68.2% K_2O and 31.8% CO_2. An artificial white compound that dissolves easily in water. Calcined potash is used in glass production. The use of potassium oxide instead of sodium oxide increases the transparency and gloss of the glass. Coloration of glass depends on the type of dye, its concentration, properties and oxidation-reduction conditions. One type of dye can color the glass in different colors depending on the process conditions and concentration. Chromium, manganese, iron, cobalt, nickel, copper, selenium, cadmium, uranium, sulfur, tellurium compounds are used as dyes to give color to glass [9-13].

Thermal properties of glass describe its ability to change as a result of heating or cooling. These properties include thermal stability, heat capacity, thermal conductivity, and thermal expansion of glass [14].

The thermal stability of the glass depends on its homogeneity and the state of the surface layer. If the glass is poorly annealed (after heat treatment), the thermal stability is low because the stress is not evenly distributed on its surface. Therefore, determining the thermal stability of glass is one of the methods of controlling the quality of glass firing. As a result of annealing the glass, its surface layer is without any defects. This increases the thermal stability of the product by 1.5-2 times. Annealing and fusible acid treatment eliminate defects in the surface layer of glass and increase its thermal stability [15].

When determining thermal stability, a sample of a glass product is heated to a certain temperature, and the heated sample is placed in cold water and its change is observed [16].

Materials and methods

Sand from the Karatobe deposit in the West Kazakhstan region was used as local raw material. A batch was prepared from the raw material from the Karatobe deposit and glass was obtained.

Determination of the thermal stability of the glass was carried out according to the Standard 25535-2013. Methods for determining the thermal stability of glass according to the standard are based on determination by heating and cooling the glass, considering the temperature difference of the heating and cooling medium.

The test is carried out on a finished product or sample with a size of 150x150 mm. Samples that have not undergone preliminary mechanical and heat treatment are taken for testing. Before the test, the samples are kept for 30 minutes in the test place at a temperature of not less than 18 ºC.

Equipment required for testing:

1) Hot water tank. The water in the tank should be changed regularly. The temperature variation of the water in the tank should not exceed 1 ºC. The volume of water should be 2 times more than the volume of the samples to be tested.

2) An electric oven heated up to 350 ºC with the ability to change the temperature. The deviation of the oven temperature from the set temperature should not exceed 1 ºC.

3) Cool water tank. The water in the tank needs to be replaced. Water temperature variation should not exceed 1 ºC. The volume of water in the tank should be 5 times more than the size of the samples.

4) A device for measuring temperature with a measurement error of ±1 ºC.

5) Sample transport containers.

6) Holders used to transport specimens.

The temperature of the test place should not be lower than 18 ºC. The temperature of the cold water in the tank should be between 5 ºC and 27 ºC. During the test, the temperature of the heating and cooling medium is determined considering the purpose of the test and the possible thermal stability of the sample.

When calculating the composition of the charge according to the specified glass composition, the composition of the charge is calculated per 100 g of net weight of sand or 100 g of net weight of glass. Usually, in practice, the composition of the charge is calculated per 100 g of net weight of glass. During such calculations, the theoretical yield of glass, losses during the glass melting process and the theoretical composition of glass are calculated. The theoretical composition of glass differs from the specified composition of glass due to the influence of contamination of raw materials. Chemically pure materials are used so that the theoretical and specified composition of the glass is the same. In this case, the theoretical and established composition of glass does not differ from each other. But it differs from the composition of the glass, which is determined by chemical analysis and depends on the conditions of the glass melting process.

Calculation of charge composition from chemically pure raw materials

The composition of raw materials used in the production of glass containing SiO_2 75%, CaO 10%, Na_2O 15% is given: sand SiO_2 100%, slaked lime $Ca(OH)_2$ 100%, soda Na_2CO_3 100%.

Calculation of the composition of the charge per 100 g of glass (Table 1).

Determination of the amount of sand:

$$100 \text{ g sand ----- } 100\% \ SiO_2$$
$$x \text{ g sand ----- } 75\% \ SiO_2$$
$$x = \frac{100*75}{100} = 75 \text{ g } SiO_2$$

Determination of the amount of slaked lime. Slaked lime decomposes during the process:

$$Ca(OH)_2 = CaO + H_2O$$

$$100\%: 74.09 \text{ g } Ca(OH)_2 \text{ ----- } 56.08 \text{ g } CaO$$
$$y \text{ g } Ca(OH)_2 \text{ ----- } 10\% \ CaO$$
$$y = \frac{74{,}09*10}{56{,}08} = 13.21 \text{ g } Ca(OH)_2$$

Determining the amount of soda. Sodium oxide passes through the glass according to the following reaction:

$$Na_2CO_3 = Na_2O + CO_2$$

$$100\%: 105.98 \text{ g } Na_2CO_3 \text{ ----- } 61.98 \text{ g } Na_2O$$
$$z \text{ g } Na_2CO_3 \text{----- } 15\% \ Na_2O$$
$$z = \frac{105{,}98*15}{61{,}98} = 25.65 \text{ g } Na_2CO_3$$

Considering that 5% of Na_2O evaporates during the process, 25.65×1.05=26.93 g of soda is obtained.

Table 1 – Theoretical composition of glass to obtain 100 g of glass

Batch composition		The amount of oxides passing into the glass, %		
Raw material	Mass, g	SiO_2	Na_2O	CaO
Sand Soda Slaked lime	75.00 26.93 13.21	75.00 - -	- 15 -	- - 10
Total	115.14	75	15	10

Results and discussion

In order to obtain colored glass, color-giving compounds were added to the composition of the charge prepared according to the calculated glass composition. When producing colored glass, not only metal oxides, but also salts of the color-giving metal were used as a color-giving compound. The coloring compounds used to obtain colored glass during the work are listed in Table 2.

Table 2 – Coloring compounds that give color to glass

Coloring compounds	Amount (%)	Color
CuO	0.1-0.2	Blue
MnO_2	0.01-0.05	Purple
S	1-2	Black
Cr_2O_3	0.05-0.1	Green
$CoCl_2 \cdot 6H_2O$	0.09-0.1	Blue
$NiSO_4 \cdot 7H_2O$	0.1-0.2	Brown

During the process of glass extraction, glass batches of two different compositions were placed in crucibles and placed in a furnace with the required temperature. After the temperature reached the desired level, the glass baking process continued for 20-30 minutes. As a result of the process, colored glass was obtained from the charge of the first composition between 800-900 ºC. And the glass from the charge of the second composition was ready at 1000-1100 ºC. Further analysis of physico-chemical properties of obtained glasses of two different compositions was carried out.

During the determination of the thermal stability of the glass in the first composition, the possible thermal stability started from 90 ºC. After that, during each repetition, the temperature of the furnace increased by 10 ºC. As a result, when the temperature reached 140 ºC, changes in the appearance of the glass were observed. When the temperature was 160ºC, the glass sample was divided into particles (Table 3).

Table 3 – The result of determining the thermal stability of colored glass in the first composition

Temperature, ºC		The condition of the sample
furnace	water	
100	18	unchanged
120	18	unchanged
130	18	unchanged
140	18	irritation was observed
150	18	the edge began to crack
160	18	divided into parts

Based on the results of the analysis, the thermal stability of colored glass in the first composition was determined:

$$\Delta T = 160\ ºC - 18\ ºC = 142\ ºC$$

According to this method, work was carried out to determine the thermal stability of colored glass in the second composition. As a result, changes in the appearance of the glass were observed at 160 ºC. And at 200 ºC, the glass was divided into particles. Based on the result, the thermal stability of colored glass in the second composition was determined (Table 4).

Table 4 – The result of determining the thermal stability of the glass in the second composition

Temperature, ºC		The condition of the sample
furnace	water	
100	18	unchanged
120	18	unchanged
140	18	unchanged
160	18	unchanged
170	18	unchanged
180	18	irritation was observed
190	18	the edge began to crack
200	18	divided into parts

Thermal stability of glass in the second composition:

$$\Delta T = 200\ ºC - 18\ ºC = 182\ ºC$$

Based on the results of determining the chemical stability of the glass in the first composition, it was determined that it belongs to the third hydrolytic class, calculating the amount of hydrochloric acid used for titration (Table 5).

Table 5 – The result of determining the chemical stability of glass in the first composition

Chemical stability	Hydrolytic class
Volume of HCl solution, ml	
0.9	3

Based on the results of determining the chemical stability of the glass in the second composition, it was determined that it belongs to the third hydrolytic class, calculating the amount of hydrochloric acid used for titration (Table 6).

Table 6 – The result of determining the stability of the glass in the second composition

Chemical stability	Hydrolytic class
Volume of HCl solution, ml	
1.5	3

Conclusion

According to the conducted research, the following conclusion was made: colored glass was obtained as a result of the addition of compounds that give color to the prepared charge. Colored glass of the first composition was ready at 800-900 ºC, and glass of the second composition at 1000-1100 ºC; physico-chemical properties of obtained colored glasses were studied. According to the thermal and chemical stability of the glass, it was determined that the thermal stability of the glass in the first composition is between 140-160 ºC, and it belongs to the 3rd hydrolytic class according to its chemical stability. The thermal stability of the glass in the second composition is about 180-200 ºC, its chemical stability belongs to the 3rd hydrolytic class.

In the course of determining the area of application of the obtained colored glass, the possibility of using it as a glaze used in the coating of ceramic products was considered.

Conflict of interest

All authors have read and are familiar with the content of the article and have no conflict of interest.

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