

## **THE APPLICATION OF BASALT IN THE MANUFACTURING OF CERAMIC GLAZES**

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### **Abstract**

*Ceramic glazes are used for the layer protection, coating and decoration of various ceramic products such as: porcelain, majolica, faience, sanitary ceramics, artistic ceramics, electro-porcelain. The application of colorless or colored glazes creates the possibility for restoration and decoration of ceramic products. Every ceramic type has a certain specific characteristic and it requires a particular type of glaze which must be in compliance with the tile.*

*This study describes the application of basalt ores from the bearing "Vrelo" on Kopaonik for faience ceramics. Investigation was performed in the aim of finding a correlation between specific characteristics of coating glazes based on basalt.*

**Key words:** *Ceramic, glaze, basalt, coefficient of thermal expansion.*

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## **1. Introduction**

Glaze is a thin glass-like layer on a ceramic tile whose basic role is to increase the physic-mechanical characteristics of the object, or in other words to disable the ability of penetration and permeability of fluids, grease and gas. Glazes are also used for surface decoration and for simplifying the maintenance of objects in clean state. On the objects made of fine ceramics, the glaze is protected by a sub-glaze color and in many cases, it is a means of decoration.

Fusible glazes with melting temperatures below 1100°C are fritted due to the solubility of some components in water such as :borax, boric acid, potash and others. Beside this, ceramic glaze composition consists of calcareous and carbonate raw material: feldspar, quartz, china clay, dolomite, CaCO<sub>3</sub>, MgCO<sub>3</sub> and others. [1-2]

All components for ceramic glazes must be clean and transparent. However, there are numerous ceramic products which are glazed by various colored glazes or are colored separately by ceramic pigments. In that case, the use of non-clean natural raw material is possible which, during melting, gives a colored glaze or the color can be made by adding certain pigments but in much smaller quantities. [3-5]

Volcanic glass has great possibilities in the application for ceramic glazes such as : pearlite, volcanic tuffs, andesite, siennite, basalts and similar. [6,7] The Republic of Serbia disposes considerable amounts of this raw material, especially basalt ore. This resulted with the idea about examining the possibility of their application in the ceramic glaze composition. This study draws special attention to this matter. [8,9]

Basalt ore from "Vrelo"- Kopaonik deposit belongs to the group of extremely hard base volcanic rocks of homogeneous constitution with high values of volumetric mass and pressure strength and very good wear-resistance. It is characterized by low water penetration, stability at low temperatures and to various aggressive compounds. The characteristics of rock are following: it is a fusible material, its melting point is about 1150°C at which a homogeneous melt is obtained, which loses the gas phase in a short period of time. By a certain cooling treatment, a compact glass-like mass is obtained and it is suitable for the fabrication of various products: basalt wool, basalt fiber, casting basalt products, basalt plastic, stone

aggregate and other products intended for mining, civil engineering, metallurgy and other necessities.

The technology of basalt ore processing is ecologically clean and the products obtained are not cancerogenous. Basalt from its deposit is of black color and has a high level of aesthetic decorative properties which make it a suitable raw material for the fabrication of ceramic glazes. [10-11]

## **2. Experiment**

### *2.1. Materials and methods*

Basalt is a volcanic rock base with the basic oxides SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, TiO<sub>2</sub> (Table 1).

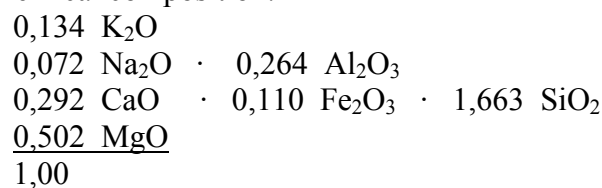
**Table 1.** Chemical composition of basalt (mass. %).

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Glow loss
1	48,92	19,99	7,91	6,38	8,39	2,89	2,39	0,35
2	48,85	13,50	8,88	10,14	8,16	2,25	3,41	0,34

Ore samples were tested by X-ray diffraction method on a X-ray diffraction meter for powder of manufacturer “Phillips”, model PW-1710. The mineral composition of the sample is: plagioclase, pyroxenes, olivines.

Quantitative mineralogical analysis was performed with the polarization microscope with reflected and throughput light of manufacturer “JENAPOL” (of company Carl-Zeiss–Jena) on petrographic devices with the identification of minerals with a brief description of their texture-structure relation. The magnification of the objective ranges from 1,65 to 50X. The system for microphotography “STUDIO PCTV” (Pinnacle Systems).

In the aim of better understanding of the mole relation of certain oxides of tested samples, their Seger formula has been given according to their chemical composition:



From the Seger's formula, it can be concluded that the basic oxides for glaze formation are present and that a certain correction is necessary in their quantitative relation. In order to obtain faience glazes, certain oxides are missing with specific purposes, such as: BaO, ZnO, B<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and a surplus of Fe<sub>2</sub>O<sub>3</sub> is present which does not exist on clean glazes or the quantity is minimum.

Based on theoretical research, the chemical composition and other characteristics of basalt, various frit and glaze are suggested. In Table 2, the prescribed composition of frit, which is used for fabrication, is shown.

**Table 2.** The prescribed composition of frit (mass. %)

Raw material	F-1/25	F-2/30	F-3/35	F-4/60
Basalt	24,03	28,30	32,71	60,00
Na-feldspar	14,68	11,16	7,80	7,50
Na <sub>2</sub> CO <sub>3</sub>	2,89	3,48	3,92	-
Boric acid	10,26	10,07	9,98	12,00
ZnO	5,97	5,80	5,80	-
CaCO <sub>3</sub>	4,42	3,62	2,94	9,00
ZrSiO <sub>4</sub>	14,43	14,16	14,02	-
Opalite	20,32	19,81	19,53	-
BaSO <sub>4</sub>	2,80	2,75	2,72	2,00
KNO <sub>3</sub>	0,96	0,94	0,93	2,00
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	-	-	-	7,50

After grinding, granulation and homogenization of the components, frits were melted at temperatures from 1350°C above in the rotational laboratory furnace in oxide atmosphere. The holding period was 1 hour at maximum temperature. After melting, frits were rapidly cooled in water and thereby the granulation was carried out.

The glazes were prepared from frits with an addition of 5% kaolin "Zetlizer" (designation: G-1/25, G-2/30, G-3/35, G-4/60). Grinding was performed by wet method in a porcelain mill with balls of fineness lower than 0,056 mm.

Biscuit baked faience tiles were used for glazing with water penetration of 18-20% by the application of watering method and emerging the product into water.

Glaze baking was performed in an industrial tunnel furnace with the maximum temperature of 980°C and rapid regime of baking which lasted 2 h and 40 min.

An attempt was made to carry out additional coloring of the obtained glazes with commercial iron, manganese and cobalt pigments. Iron pigments in small quantities up to 4% can result in good and homogenous dark chocolate color. Manganese pigment colors glazes from gray to black color, depending on the quantity and glaze type. Cobalt pigment in the quantity of 2% colors glazes in gray to dark blue colors depending on the quantity and glaze type. Cobalt pigment is not suitable for this glaze type because it does not give the anticipated blue color that is characteristic of this pigment type. The best results are obtained with iron pigment. Instead of commercially expensive iron pigments, iron ore or other can be used for this glaze type.

The obtained glazes were subject to conventional testing: temperature change, thermal stability of the glaze, chemical and primary resistance, hardness and thermal expansion coefficient of the glaze.

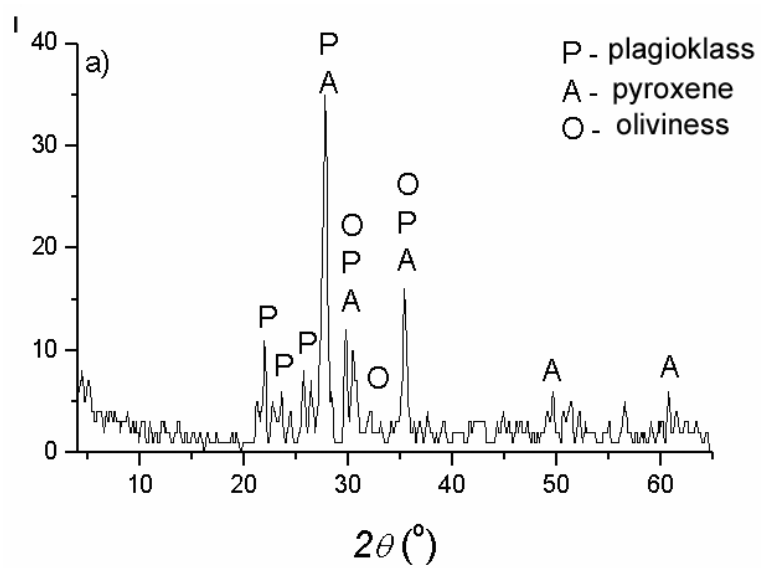
### **3. Results and discussion**

Basalt samples used for the manufacturing of the glazes represent a compact, solid rock from massive to fluid structure. It is a dark green color without visible cracks. X-ray structure analysis of basalt is illustrated in the X-ray diffraction (Fig.1). In Fig.1 it can be seen that the sample is mostly consistent of primary plagioclase minerals, while pyroxenes (augite) and olivines are less present.

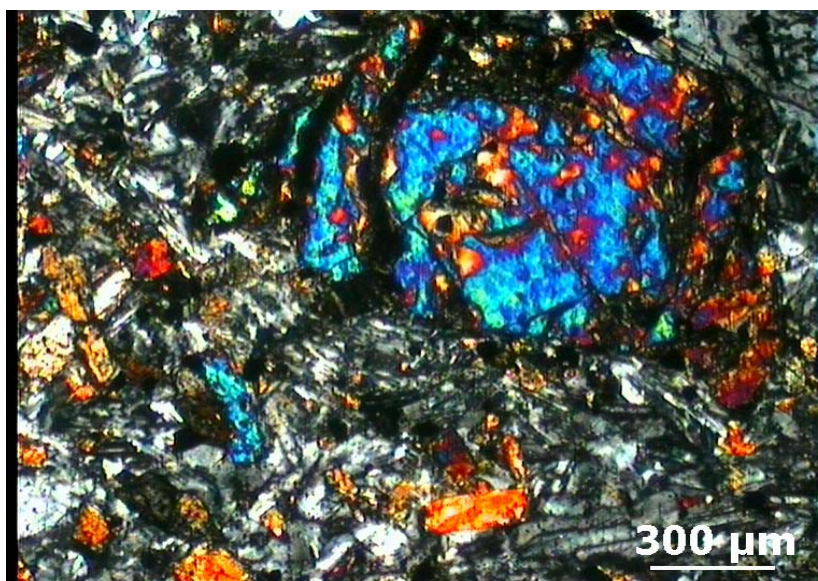
The base of tested sample is made of micro crystal plagioclase (basic mass) of microlytic structure. Olivines were determined from phenocrystals, elongated pyroxines, and less frequent basic plagioclase. Samples are partially hematite brown. The rock is presented as olivine-pyroxene basalt, fig. 2.

The obtained frits based on basalt (composition according to Table 2) are well melted, opaque and without an embedded gas phase. Only frit F-4/60 has a shiny black color.

The ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3$  is increased in the obtained glazes ( $\text{SiO}_2:\text{Al}_2\text{O}_3=9,55$ ), with the exception of glaze G-4/60 where it remained almost on the same level as basalt ( $\text{SiO}_2:\text{Al}_2\text{O}_3=5,71$ ). The last glaze is far more of base character in comparison to the first three glazes.



**Fig. 1.** X-ray diffraction of a powder basalt sample



**Fig. 2.** Phenocrysts of lozenged pyroxenes. Permeable light, *II N*.

All glazes belong to the melting temperature range from 980-1020°C and the temperature change of 1000°C. The linear thermal expansion coefficient is  $7,10-7,35 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . After baking, glaze G-1/25 and G-2/30 are of light color and somewhat darker cream color, glaze G-3/35 has a chestnut color and glaze G-4/60 has an ocher yellow color. All glazes are opaque ink and even glaze G-4/60, even though it doesn't contain ZnO and ZrO<sub>2</sub> in its composition.

#### **4. Conclusion**

Based on the complete investigation that was concerned with application of basalt in obtaining a ceramic glaze, whose share in the prescription of tested glazes ranges from 25-60%, it can be concluded that all four glazes are applicable for glazing faience ceramics with the glaze baking temperature ranging from 980-1020°C. It was experimentally proved that the mentioned components—basalt rock from “Vrelo” deposit on Kopaonik are suitable for obtaining low-temperature frit faience glazes, predominantly colored but transparent also. Frit temperatures range from 1300-1350°C and are lower by 50-100°C in comparison with classical compositions. Based on these raw materials, stable, high quality and very cheap frit glazes can be obtained for faience ceramics.

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