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ANALYSIS OF CHANGE IN THE DECORATIVE PROPERTIES OF GRANITES UNDER THERMAL EXPOSURE

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Експериментально досліджувалися зразки з дев'яти родовищ гранітів, які видобувається в Україні. Випробування зразків гранітів проводилося високими температурами 200, 400, 600, 900 °C.

Всі представлені граніти показують зміну кольору поверхні при температурі від 200 °C і вище. Поведінка гранітів з нагріванням залежить від їх мінерального складу, структури та текстури.

Поверхні всіх дослідних зразків стали світліше, деякі зразки гранітів втратили насиченість кольорів. При нагріванні зразків до 900 °C природного каменю найбільше зростання компоненти L (зображення зразків каменю світлішає) кольорової системи CIELab відбулося у зразках гранітів Cardinal Grey та Carpazi відповідно на 42 та 44 %. Найменше зростання компоненти L при нагріванні зразків до 900 °C відбувається у гранітах Grey Ukraine, L відповідно на 4 та 8,5 %.

Вплив температури на зразки з червоного граніту візуально менш виражений, оскільки як свіжі, так і нагріті, зразки мають подібний червоний колір. Завдяки вмісту апатиту та флюориту зразки граніту Flower of Ukraine набувають рівномірного фіолетово-рожевого кольору при температурі 900 °C. В сірих гранітах при нагріванні з'являються почервоніння, які переважно сконцентровані навколо слюди та інших мінералів, які багаті Fe. На зеленому граніті Verde Oliva з'являються руді плями при температурі 200 °C. При нагріванні до 900 °C руді плями займають 67 % площі зразка.

Найбільшу зміну кольору отримали граніти, в яких відбувся фазовий перехід темноколірних мінералів (біотиту та піроксену) в поліморфні мінерали. Це надало зразкам гранітів світлішого кольору, так як мінерали змінили колір з чорного на сірий чи білий. Відтінки білого кольору надав кварц, в якому при нагріванні з'являлися білі мікротрішини.

Помітні естетичні пошкодження поверхні зразків природного каменю починаються при температурах від 200 до 400 °C. Таким чином, вогонь з температурами нижче цього порогу можна вважати «безпечним» з точки зору естетичного пошкодження, якщо врахувати тільки коефіцієнт нагріву вогню і виключити золу і гази

Ключові слова: граніт, високі температури, декоративність природного каменю, мінеральний склад, структура граніту

1. Introduction

Physical appearance of a natural facing stone is important for its use as a facing material. People built a considerable number of architectural monuments using facing rocks. Taking into consideration their considerable age, questions arise regarding their restoration [1]. There are certain possible problems: deposits ceased to develop, or deposits develop other horizons. A color of natural stone may have different shades at different terraces in this case.

In addition, aggressive environmental factors change decorative properties of facing. Namely, reddish-brown spots appear on surface of natural stone, it changes its color. Therefore, there is a need to control decorative properties of natural stone. One of the ways to change decorative properties is the influence of high temperatures. For example, high temperatures are able to accelerate iron oxidation or to change saturation of colors.

In addition, natural stone is a fire-resistant building material. Nevertheless, fire can lead to irreversible damage to buildings both in structural and aesthetic terms. The structure and texture of natural stone determine its behavior under heating [2]. Granites can exhibit intense changes in surface properties such as gloss, color, or roughness [3], which can lead to a decrease in decorative properties [4]. Properties of stone surface depend on a mineral composition, structure, texture and treatment. For example, a color of a natural stone depends more on a mineral composition and structure. It depends less on surface treatment [5]. Questions on restoration of buildings arise after fires. It is possible to determine values of temperatures, which affected facing of building, by changes in the color of natural stone. This makes possible to determine suitability of natural stone for operation or to prepare plates of fresh granite for restoration of the most affected areas of a building by heating. Therefore, there is a need for studies on changes in decorative properties of granites under thermal influence.

2. Literature review and problem statement

There are problems with selection of natural stone for reconstruction of external facings of buildings. For example, reddish-brown spots appear under the influence of an aggressive environment due to iron oxidation. Paper [6] presents a methodology for intensification of oxidation of iron in labradorite by means of high temperature. This makes it possible to change decorative properties of fresh labradorite to the desired values. However, the study is for labradorite only. Reddish-brown spots appear on surface of natural stone if one heats it or exposes to aggressive environments. Oxidized iron appears on surface of samples of labradorite [6] and limestone [7] in large amount. The amount of oxidized iron, which appears on surface of granite samples, is less [4]. Authors of studies [7] and [4] did not calculate an area of oxidized sites. Thus, the study does not make it possible high-precision control of decorative properties by means of high temperature.

The main factor, which affects building materials during fire, is heat emitted by flame. This, in turn, leads to a change in decorative properties of natural stone. There is an increase in the value of *L* component (an image of samples of stone becomes lighter) of the CIELab color system in most granites [4]. However, some granite samples tend to reduce the value of *L* component. *A* and *b* components increase, but an increase is different for each stone. There is a decrease in *L* component at the temperature range of 400–600 °C in some samples. Authors measured the color by MINOLTA CR-200 spectrophotometer with D65 illuminator and a bundle of diffuse xenon light with a diameter of 8 mm. This measurement method may give an error in determination of the color due to complexity of determination of the representative color value in heterogeneous material, where a grain size may exceed the diameter of a device.

However, the study showed that the presented granite samples have different changes in decorative parameters under an influence of high temperatures. Therefore, the issues related to the change in the color of granite in Ukrainian deposits under heating are still expedient.

3. The aim and objectives of the study

The objective of the study is investigation and establishment of the basic dependencies of a change of color coordinates of facings of natural stone in the CIE Lab system caused by the influence of high temperatures. The study will give possibility to control decorative properties of natural stone and to receive facing articles with given decorative properties.

To accomplish the aim, the following tasks have been set:

– to determine temperature, which makes aesthetic damage to surface of samples of natural stone noticeable;

– to determine quantitative values of color coordinates in the CIE Lab system of polished surface of samples under heating;

– to investigate a color change in samples of granite under heating.

4. Materials and methods to study the influence of high temperatures on decorative properties of granite

We studied the samples of decorative natural stone from nine deposits located in Ukraine (Fig. 1) with the following commercial names: Rosso Toledo (RT), Verde Oliva (VO), Leopard (L), Carpazi (C), Maple Red (MR), Gray Ukraine (GU), Flower of Ukraine (FU), Rosso Santiago (RS) and Cardinal Gray (CG). All granites have different mineralogy, texture and physical properties.

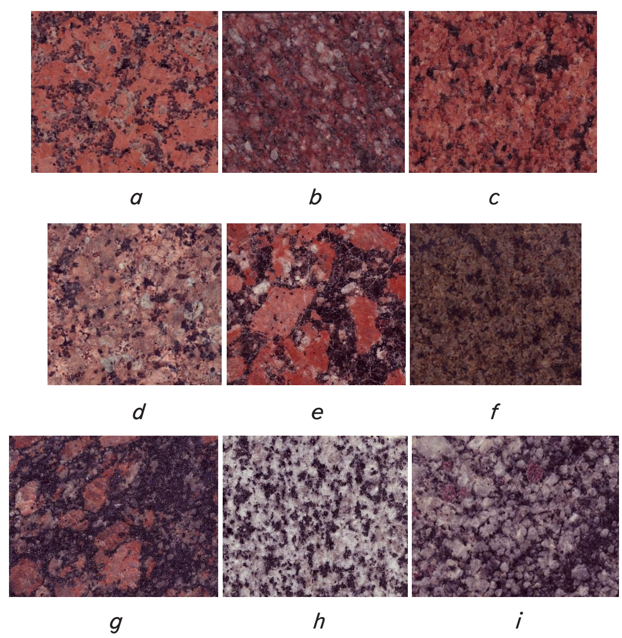


Fig. 1. Samples of undamaged natural stone: *a* – RT; *b* – C; *c* – MR; *d* – FU; *e* – RS; *f* – VO; *g* – L; *h* – GU; *i* – CG

The feature of Rosso Toledo granite is its exclusive homogeneity and absence of xenoliths and pegmatite veins.

The granite consists of microcline – 65 %, plagioclase – 10 %, quartz – 20 %, biotite – 4 % and other minerals – 1 %. Crystals of potassium spar of sizes up to 2–3 cm painted in red-brown tones determine the color of granites. There are crystals of black biotite and yellowish-gray plagioclase (orthoclase) uniformly embedded on a red background. Granites are coarse-grained and porphyry-like.

Verde Oliva granite is solid gray, greenish gray, mostly dark green rock macroscopically. It has massive texture and unevenly medium-grained structure. It has the following mineral composition: microcline-perthite – 40–63 %, plagioclase – 0–20 %, quartz – 25–40 %, hornblende – 1–10 %, biotite – 1–7 %, pyroxenes – up to 2 %, apatite – 0–2 % and fluorite – 0–1 %. Granites are highly aluminous in terms of petrochemistry.

Leopard has the following mineral composition: microcline – 18–25 %, plagioclase – 20–25 %, quartz – 20–25 % and biotite – 7–13 %. There are numerous scales of brown biotite. It also contains secondary minerals, sericite and epidote in limited amounts.

Carpazi granites are homogeneous and unevenly medium-grained. Their texture is massive. They have the following mineral composition: orthoclase and microcline – 40 %; plagioclase – 24 %; quartz – 30 % and biotite – 5 %. The texture of granite is mosaic; it has large red specks of feldspar, which are sharply distinguished by glittering areas of unity, as well as small, fine-grained deposits of red apatite.

Maple Red Granite is evenly medium-grained. It consists of pink and red feldspars – up to 65 %; colorless or smoky quartz – 30 % and biotite and other minerals – 5 %. A picture is absent in a monochromatic color. We perceive macrostructure only, which has seeds of biotite uniformly embedded in red mass of feldspar.

Gray Ukraine granodiorite has a rich and even color. The color remains the same in different lots. The mineral composition of Gray Ukraine is as follows: microcline 15–30 %; plagioclase – 35–55 %; quartz – 10–25 %; biotite – 5–15 % and other minerals – <1 %.

Flower of Ukraine granites are homogeneous in mineral terms. They contain quartz – 10–40 %, plagioclase – 5–25 %, microcline – 35–84 %, biotite – 0–7 %, hornblende – 0–7 %. They also contain secondary chlorite minerals. Their content does not exceed one percent. There are also the following accessories: apatite, zircon and orthite and an ore mineral represented by magnetite. The colors of granite are pink, grayish-pink and pale pink. Pink feldspars in the form of individual grains of 2–5 mm in size and large oval shapes create the main color. There are stand-alone tabular crystals of white and grayish-white feldspar distinguished. Black and greenish-black grains up to 5–10 mm in size supplement the color set. The texture of granite is massive.

Rosso Santiago granite is porphyry-like, garnet-biotite. Granite has a pinkish-red color, a massive composition and a large-grained structure. Large crystals of feldspar reach 3 cm in length and 4–5 cm in width. Rosso Santiago has the following mineral composition: potassium feldspar – 15–60 %; plagioclase – 10–25 %; quartz – 30–60 %; biotite – 2–15 %, garnet – 3–15 %, apatite, zircon and muscovite – less than 1 % and carbonates – less than 1 %. The disadvantage of this granite is presence of large grains of garnet (up to 0.5 cm). They affect the quality of polished surface negatively, because garnets crumble out.

Cardinal Gray granite is pegmatoid granite. It is gray and evenly granular. It has a medium-grained structure. It has the following mineral composition: plagioclase – 4–5 %; microcline – 5–7 %; quartz – 30–35 %; cordierite – 3–5 %; garnet – 1–2 % and biotite – 10 %. The feature of Cardinal Gray granites is presence of a cluster of garnet and xenoliths of biotite gneiss.

We digitized faceplates of natural stone samples with Canon CanoScan LiDE 700F scanner. We used IT-8 product produced by Agfa for correction of color representation errors. This makes it possible to use this device for various color measurement with high precision.

We heated granite samples at a rate of 1 °C/min to 200, 400, 600, 900 °C in the electric oven. We exposed granite samples for 1 hour at a given temperature, and then cooled them to the temperature of 20 °C at a rate of 1 °C/min. The rate of a temperature rise was low to achieve maximum temperature effect.

We measured color on digital images. The measurements were perdormed in the CIE Lab system (UNE-EN ISO 105-J03: 2007). L component is a parameter of color lightness (saturation), which ranges from 0 (black) to 100 (white). A component is a chromatic parameter, which changes from green (negative) to red (positive). B component is a chromatic parameter, which changes from blue (negative) to yellow (positive). We introduced ΔE as a general color change to compare changes before and after the tests, if possible, as follows:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}.$$

The data were processed using the MdiStones software. Paper [8] presents its operation algorithm.

5. Results of assessment of stability of granites under high temperatures

5. 1. General characteristics of investigated rocks

We divided all samples of natural stone into three groups by color.

1st group. Gray granitoids: GU and CG. Combination of whitewash feldspars and dark ferro magnesites (minerals of the biotite group, amphibole or pyroxenes) determine general appearance of gray granites. The predominance of plagioclases gives gray color of various shades to the rocks [9].

2nd group. Red granites: RT, C, MR, FU, and RS. They contain potassium feldspars, which give red and pink color to granitoids. The microcline has a color from pinkish-red to yellowish brown, depending on the quantitative ratio of the hematite phase and goethite phase, which are simultaneously present in the microcline matrix [9].

A metamorphic transformation of granitoids occurs under influence of radioactive fields on rocks of the 2nd group. There is a shift of the phase ratio towards hematite, and, as a result, there is reddening of microclines and rocks. On the contrary, under the influence of hydrothermal solutions, the phase ratio shifts towards goethite, which leads to shades of yellow and brown.

3rd group. Greenish color of plagioclases determines a green color of VO granites. Plagioclases make up 50 % of the mineral composition of the rocks. Plagioclases give white, light gray and gray to black shades, sometimes greenish, yellowish and grayish-green (due to micro inclusions of green iron-containing silicates) colors to granitoids, because of secondary changes in plagioclase – formation of chlorite and epidote [9].

5. 2. Determination of temperature, which causes noticeable aesthetic damage to surface of samples of natural stone

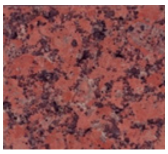
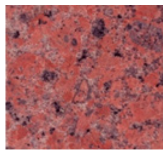
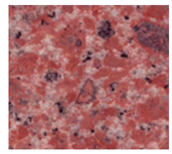
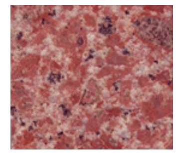
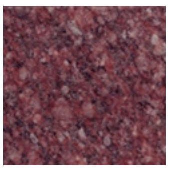
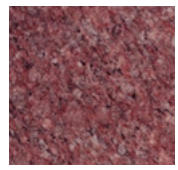
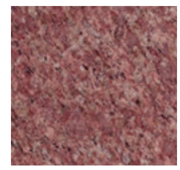
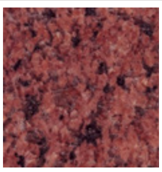
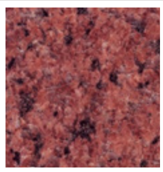
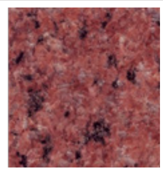
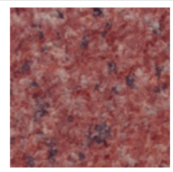
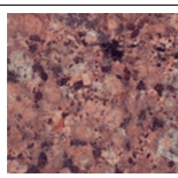
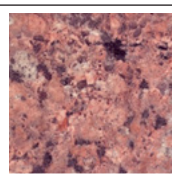
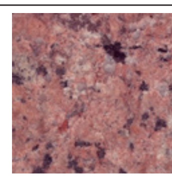
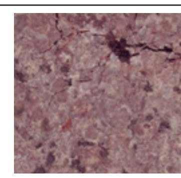
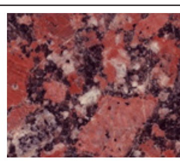
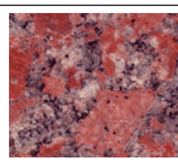
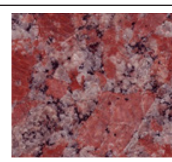
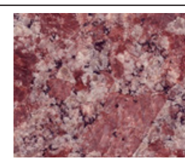
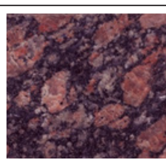
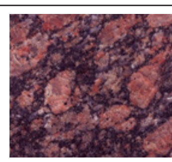
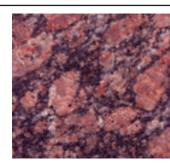
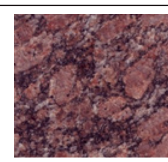
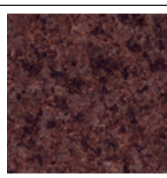
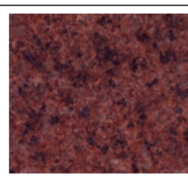
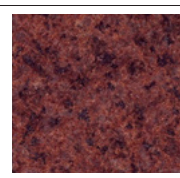
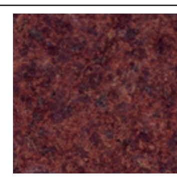
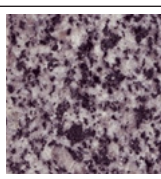
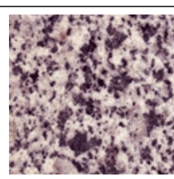
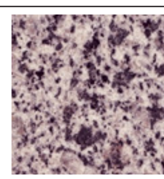
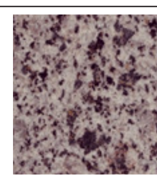
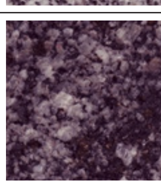
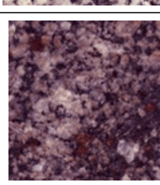
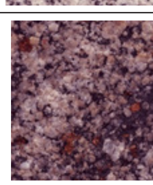
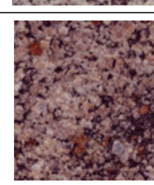
a) Changes in granites from the 1st group.

We observed no significant changes on the images of samples of gray granitoids at a temperature of 200 °C (Table 1).

Samples of GU granodiorite at a temperature of 400 °C become lighter. There is a decrease in dark-colored minerals at a temperature of 600 °C on samples of natural stone and small reddish-brown spots appear. Granodiorite samples show an increase in reddish-brown spots at an average temperature of 600 °C, the image darkens.

Table 1

Physical appearance of stone samples at different temperature of influence

Deposit name	Temperature of heating, °C			
	200	400	600	900
RT				
C				
MR				
FU				
RS				
L				
VO				
GU				
CG				

There is an increase in minerals of gray color at the temperature of 400 °C on surface of samples of CG granite. Cells of oxidized iron appear in places where ore minerals appear. It is possible to see the change in a color of garnet. There is a decrease in a number of dark-colored minerals at the temperature of 600 °C on surface of samples. Garnet minerals change their color from brown to brownish-red. Minerals of gray color dominate on surface of samples at the temperature of 900 °C. The number of reddish-brown spots almost does not increase.

b) Changes in granites from the 2nd group.

Red granites show a progressive color variation. There is a change in a color of black minerals to gray color at a temperature of 400 °C on RT granite. These minerals become white at 600 °C. The red color of minerals almost does not change at a temperature of 900 °C. Black minerals become gray at 900 °C on C and MR granites. Minerals of red color become lighter.

Dark-colored minerals change their color to gray at a temperature of 400 °C on FU granite. Minerals with a dark pink color change to red-orange; the image of a sample of natural stone becomes lighter. Minerals of a red-orange color change their color to dark pink at the temperature of 600 °C. The image becomes darker. Minerals of dark pink color change it to pale-violet color at the temperature of 900 °C. The image becomes darker.

Dark-colored minerals become gray, minerals of red color become lighter at a temperature of 400 °C in RS granite. Minerals of light red color change their color to dark red at a temperature of 600 °C. Minerals of dark red color change their color of claret red at a temperature of 900 °C. Gray minerals become lighter and the color becomes close to white.

Dark-colored minerals become gray at a temperature of 400 °C on L granite, feldspar almost does not change its color and spots of claret red color appear due to garnet.

Dark-colored minerals become white-gray more intensively at the temperature of 600 °C. Reddish-brown spots appear on surface of a natural stone.

Red minerals change their color to claret red at the temperature of 900 °C. Reddish-brown spots appear. The image of the sample of natural stone acquires a homogeneous shade of pale claret red color with gray-white mineral inclusions.

c) Changes in granites from the 3rd group.

Dark-colored minerals show a deviation from black to brown at 900 °C. Reddish-brown spots begin to appear at the temperature of 200 °C on surface of VO granite. They replace a green color. The sample saves green color. The green color of the granite changes to the red color at the temperature of 400 °C. There is an increase in reddish-brown spots and a decrease in dark-colored minerals on surface of the stone samples under heating to 900 °C.

5. 3. Determination of quantitative values of color coordinates in the CIE Lab system of polished surface of samples under heating

A and *b* parameters give color to a stone. Gray granitoids show the average *a* value – from 23 to 25 on the image (Fig. 2).

The average value of *b* on gray granites – lies between –18 and –19 on the image (Fig. 3). Green granite shows the average value on the image – b=–9, a=32.

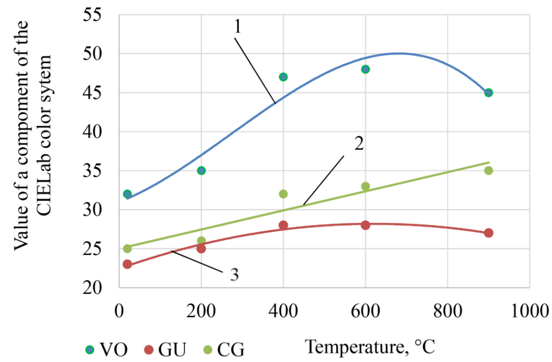


Fig. 2. Dependence of a component of the CIELab color system on heating temperature for green and gray granites:
1 – $y=-8E-08x^3+6E-05x^2+0.0205x+30.991$ ($R^2=0.9383$);
2 – $y=0.0122x+25.006$ ($R^2=0.8979$);
3 – $y=-2E-05x^2+0.0186x+22.435$ ($R^2=0.9648$)

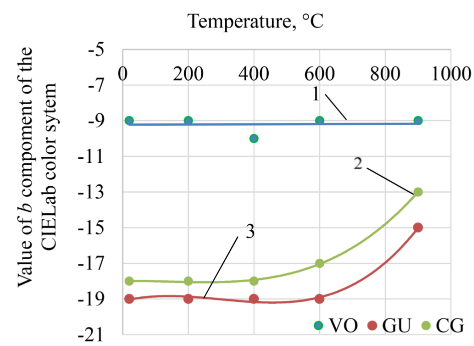


Fig. 3. Dependence of *a* component of the CIELab color system on heating temperature for green and gray granites:
1 – $y=5E-05x-9.2216$ ($R^2=0.915$);
2 – $y=1E-08x^3-5E-06x^2+0.0002x-17.986$ ($R^2=0.9995$);
3 – $y=2E-08x^3-2E-05x^2+0.0045x-19.118$ ($R^2=0.9956$)

Red granitoids have an average *a* value from 31 to 55 – in the image (Fig. 4).

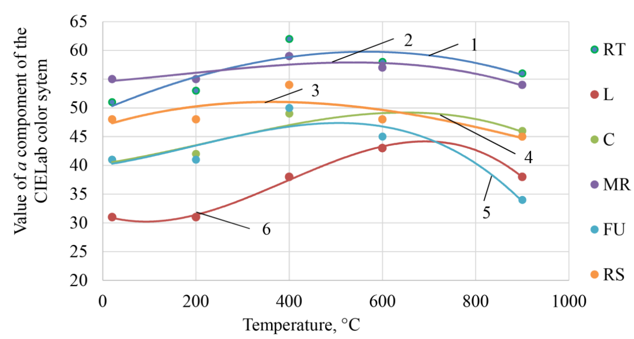


Fig. 4. Dependence of *a* component of the CIELab color system on heating temperature for red granites:
1 – $y=-5E-09x^3-3E-05x^2+0.0341x+49.64$ ($R^2=0.8398$);
2 – $y=-2E-08x^3+1E-05x^2+0.0065x+54.545$ ($R^2=0.8402$);
3 – $y=1E-08x^3-4E-05x^2+0.0244x+46.876$ ($R^2=0.8011$);
4 – $y=-4E-08x^3+3E-05x^2+0.0124x+40.308$ ($R^2=0.8492$);
5 – $y=-7E-08x^3+4E-05x^2+0.0121x+40.037$ ($R^2=0.8539$);
6 – $y=-1E-07x^3+0.0002x^2-0.0249x+31.323$ ($R^2=0.9949$)

The average value of *b* color component for red granites lies in the range from –9 to –16 (Fig. 5).

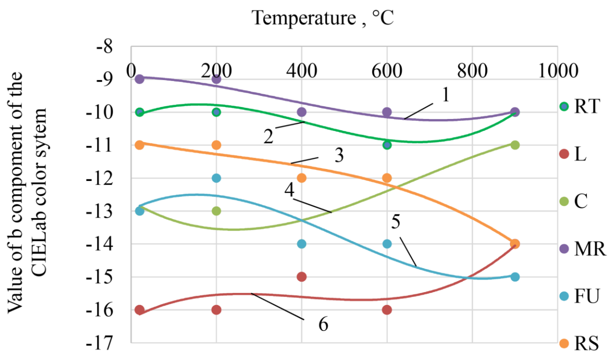


Fig. 5. Dependence of *b* component of the CIELab color system on heating temperature for red granites:
1 – y=6E–09x^3–7E–06x^2–0.0003x–8.9304 (R^2=0.8752);
2 – y=2E–08x^3–2E–05x^2+0.0054x–10.162 (R^2=0.806);
3 – y=–5E–09x^3+4E–06x^2–0.0025x–10.871 (R^2=0.9574);
4 – y=–1E–08x^3+2E–05x^2–0.0078x–12.695 (R^2=0.8089);
5 – y=2E–08x^3–2E–05x^2+0.0064x–12.963 (R^2=0.8114);
6 – y=2E–08x^3–2E–05x^2+0.0069x–16.261 (R^2=0.7794)

L parameter gives the value of lightness or saturation of a color. The lightest granites are gray GU granite (Fig. 6) *L*=47, red FU granites (Fig. 7) *L*=43, RT with *L*=38.

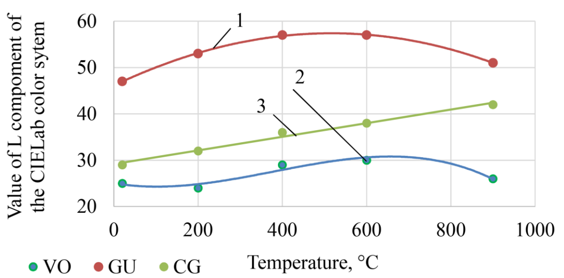


Fig. 6. Dependence of *L* component of the CIELab color system on heating temperature for green and gray granites:
1 – y=–1E–09x^3–4E–05x^2+0,0434x+46,11 (R^2=0,9991);
2 – y=–8E–08x^3+9E–05x^2–0,0154x+25,034 (R^2=0,9138);
3 – y=0,0147x+29,167 (R^2=0,9875)

We can attribute the following granites to interim ones: RS (*L*=33), MR (*L*=32) and C (*L*=30). They have alkaline feldspars, which have colors from grayish to reddish (Fig. 7).

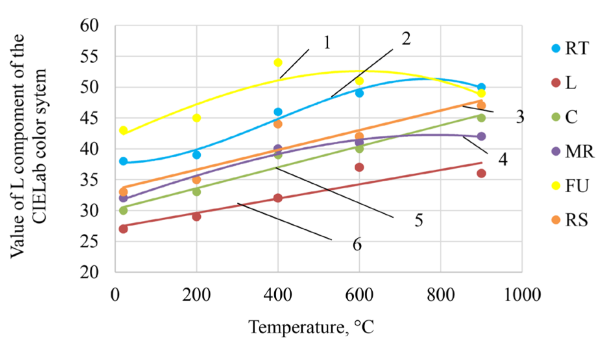


Fig. 7. Dependence of *L* component of the CIELab color system on heating temperature for red granites:
1 – y=–2E–08x^3–1E–05x^2+0.0298x+41.772 (R^2=0.7925);
2 – y=–6E–08x^3+7E–05x^2–0.0015x+37.749 (R^2=0.9794);
3 – y=0.016x+33.423 (R^2=0.8434);
4 – y=–8E–09x^3–5E–06x^2+0.0228x+31.36 (R^2=0.9809);
5 – y=0.017x+30.195 (R^2=0.9642);
6 – y=0.0116x+27.276 (R^2=0.8502)

We can attribute the following granites to dark granites: CG (*L*=29), L (*L*=27) and VO (*L*=25).

Studies show that all color parameters of surface of stone samples change under the influence of high temperature. *L* parameter increases in most samples. This dependence is linear on samples of C, CG and RS granites. *L* component is the greatest (*L*=54) at the temperature of 400 °C on FU sample. It decreases to 49 with further heating to 900 °C. The samples of GU and VO natural stone behave similarly. *L* component is the greatest at 400 °C. It remains the same until 600 °C. And it decreases at 900 °C. The value of *L* component increases to the temperature of 600 °C rapidly on samples of RT, L, and MR natural stone. The rate of growth of values of *L* parameter decreases at the temperatures above 600 °C. *L* parameter increases by 1 only in the range of 600–900 °C on RT, L, MR samples. When we heat the samples up to 900 °C, the greatest growth of *L* component occurs on samples of CG and C granites, by 42 and 44 %, respectively. The smallest increase in *L* component occurs on GU and L granites, by 4 and 8.5 %, respectively, when we heat the samples to 900 °C.

There is a decrease in *b* color component on samples of MR, FU, RS granites.

There is an increase in *b* color component on samples of L, C, GU, CG granites. There is also an increase in *a* color component on samples of C, GU, CG granites.

There is a decrease in *b* color component in the range of 400–600 °C on samples of VO and RT granites, and there is a comeback to initial values at 900 °C.

There is an increase in *a* color component under heating to a temperature of 400–600 °C on samples of VO, L, RS, RT, MR, FU granites, and there is a decrease in this parameter under further heating.

5. 4. Investigation of the color change on samples of granite under heating

Δ*E* is a general color change parameter in the CIE Lab system. Δ*E*>2 values are quite noticeable for observation by a naked eye and therefore we consider them as a sign of "aesthetic damage" (that is, a color will be different after heating/fire). Δ*E* values (Fig. 8) are near the specified threshold on the samples of granites heated to 200 °C, except GU granite (ΔE=6.32).

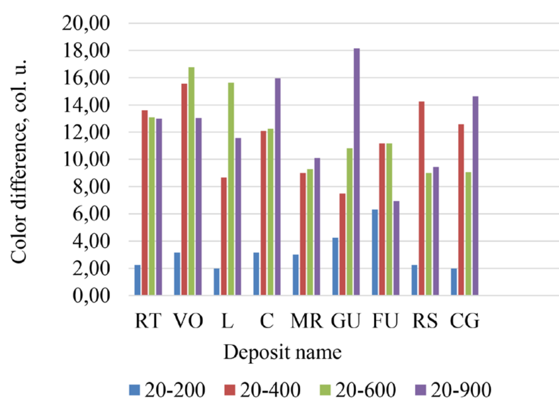


Fig. 8. ΔE value of the CIELab color system for heated samples of stone

ΔE value is the lowest on L and RS granite samples, it is ΔE=2. ΔE value is the highest on the samples of CG, C, VO granites, it is ΔE=3.16. Therefore, the color change is almost invisible on most samples heated to 200 °C. Conversely, the color change is visually noticeable at all other test temperatures (400, 600, 900 °C), where ΔE>3 for all cases. There is the greatest increase in Δ*E* on all natural stone samples at 400 °C. Red FU granite with green inclusions and green VO granite have the greatest value of Δ*E* (Δ*E*=12.9–13.0, respectively). Δ*E* values decrease at 600 °C. Red granites show the highest ΔE values in relation to values at 400 °C. Δ*E* increases with temperature, the maximum values show gray CG granite samples – Δ*E*=17.1 and red C granite – Δ*E*=15.9. There is a sharp increase in Δ*E* at the temperature of 400 °C on all granite samples, and there is a decrease of Δ*E* at 600 °C. Δ*E* parameter increases slightly on most of the stone samples, except for FU samples, at the temperature of 900 °C.

6. Discussion of the obtained results on assessment of a change in decorative properties of granite under thermal influence

There are fewer studies on the influence of high temperatures on changes in appearance of granites than studies on other types of stones. These changes relate to mineralogy and texture. The connection between development of color and high temperatures can give information on temperature of fire [10]. Cracks close when we heat granite to 130 °C [11]. Cracks open again due to expansion of minerals if temperature increases further [12].

There is a decrease in dark-colored minerals at a temperature of 400 °C on samples of natural stone. Small reddish-brown spots appear due to oxidation of iron in iron-containing minerals. Some studies indicate that reddening of stone occurs at a lower temperature. For example, authors of a paper [13] found that there was a reddening at the temperature of 200 °C in yellow trachyte. This color change occurred due to insignificant oxidation of iron contained in ferromagnesic minerals and some red feldspar. Different iron-containing minerals lead to a different color change, as the temperature of oxidation increases. For example, hematite and iron hydroxides produce intense reddening of stone, while chlorite becomes yellowish firstly [14]. Therefore, the color change in iron-containing minerals depends on a type of mineral and temperature of oxidation.

VO, L, CG and GU granites have the most intense color deviations. Fe oxidation contributes to this. Ferromagnesic minerals of the biotite group and amphiboles contain high Fe share. These minerals actually show the most noticeable change in color from black and green to brown and golden shades after heating. It is possible to estimate Fe oxidation intensity in dependence on temperature by the relative area of reddish-brown spots, which appear on surface of stone samples (Fig. 9).

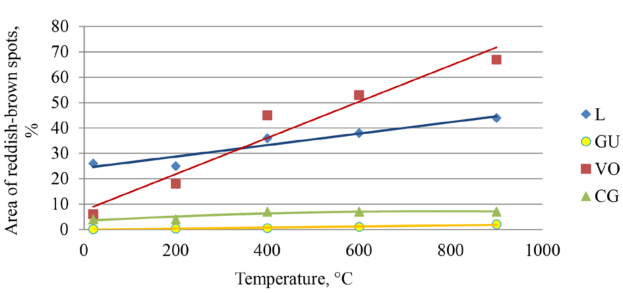


Fig. 9. Dependence of the area of reddish-brown spots on surface of a sample in dependence on temperature

Fig. 9 shows that green VO granite and pinkish-gray L granite have the largest content of Fe. The oxidation of Fe occurs uniformly.

Reddish-brown spots begin to appear on surface of VO granite at the temperature of 200 °C. They replace a green color. The change in the color of stone becomes noticeable from 300 °C due to oxidation of iron-containing minerals between 205 °C and 300 °C [15]. The green color of granite changes to the red one at 400 °C. The appearance of reddish-brown spots on green VO granite is the result of oxidation of minerals of the biotite group and alkaline feldspar. They give a grayish-green shade to natural stone. Both minerals change their colors under heating. Minerals of the biotite group become golden, red alkaline feldspar turns into garnet-red one.

Fe oxidation does not affect the color of samples of some granites, for example, MR and RS granites, so Fig. 9 does not show them.

Reddish-brown spots appear in areas of placement of garnet on CG samples. Garnet turns from dark brown to brown at 200 °C. The color of this mineral lightens up to a grayish brown color as temperature rises.

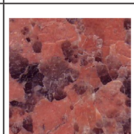
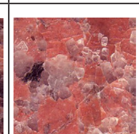
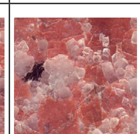
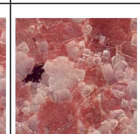
The results obtained from the calculation of the area of reddish-brown spots provide an opportunity to restore buildings affected by aggressive environment or high temperature. If one knows the required specific area of reddish-brown spots, one can create similar pieces of a facade of a building by heating of stone to the desired temperature.

Studies show that all color parameters of surface of stone samples change under high temperature.

Transgranular cracks and new intraregular cracks appear in quartz of granite samples (Table 2). This is consistent with a work [16]. That is, it happens earlier than in sandstones, where development of microcracks in quartz and alkaline feldspar occurs at the temperature above 600 °C [17].

Table 2

Physical appearance of fragments of granite samples after heating

RT granite	Temperature of heating, °C			
	200	400	600	900
Appearance of a stone sample				

Microcracks can cause appearance of a dark gray color on some granites, such as CG, GU, FU and L, and whiter colors on some granites, such as RS, RT, GU (Fig. 10).

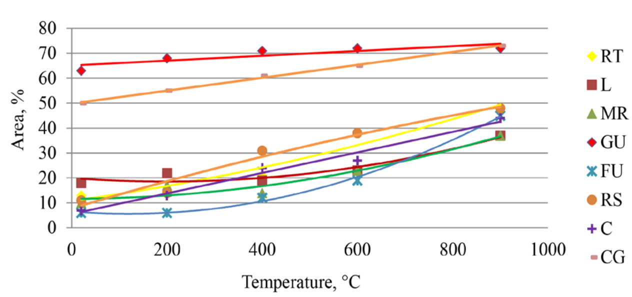


Fig. 10. Dependence of the area of gray and white spots on surface of samples on temperature

B color component, which passes through a yellow color, changes on gray CG and GU granites. The change is visible to a naked eye. This coincides with the results obtained for gray trachyte, which becomes yellow [13].

Samples of GU granodiorite lighten at the temperature of 400 °C due to the phase transition of hornblende and minerals of the biotite group from black and gray to white-gray. The image becomes darker at the temperature of 600 °C due to the color change in minerals from white to gray.

Microcracks appear in quartz at 600 °C due to alpha-beta-transition at 573 °C. Cracks become more noticeable. Quartz microcracks provide a more white shade to surface of all granites. The increase in *L* component confirms this. Feldspars showed also development of cracks after heating to this temperature, which confirms a work [10]. Color changes differ slightly from 400 to 600 °C for all granite parameters.

Dark-colored minerals change their color to gray, feldspar changes its color from dark-pink to red-orange one, the image of the sample of natural stone is lighter at the temperature of 400 °C on FU granite. Feldspar changes its color from red-orange to dark-pink at 600 °C. Due to this, the image becomes darker. Minerals of chlorite merge with minerals of feldspar and form a pale-violet color at the temperature of 900 °C.

Hornblende and minerals of the biotite group become gray at 400 °C on RT granite. They acquire a white color at 600 °C. The color of potassium feldspar almost does not change at the temperature of 900 °C. Minerals of the biotite group become gray at 900 °C on C and MR granites. Feldspar minerals become lighter.

Smoky quartz becomes gray; feldspar almost does not change its color at the temperature of 400 °C on L granite. Spots of claret red color appear due to garnet.

Smoky quartz becomes white-gray more intensively at the temperature of 600 °C, reddish-brown spots appear due to spinel-like oxides and high-iron silicates.

Red feldspar changes its color of claret red at the temperature of 900 °C. Reddish-brown spots appear due to iron-containing minerals. The image of a sample of natural stone acquires a homogeneous color of pale claret red with gray-white inclusions of quartz.

Dark-colored minerals become gray at the temperature of 400 °C on RS granite, red feldspar becomes lighter. Light-red feldspar changes in color to dark red at 600 °C. Dark-red feldspar changes color to claret red at the temperature of 900 °C. Quartz becomes lighter. It approaches white color.

There is development of cracks observed between 600 °C and 900 °C. Some of RT and FU granites have serious damage (although measurements are still possible). The high content of minerals of the biotite groups and plagioclase influence the destruction.

L color component increases on the samples of C, CG, RS, RT, L and MR granites, due to high quartz fracture, which gives whitish color. A decrease in *L* color component on FU, VO, GU samples of granites occurs due to transition of a color of quartz and feldspar to gray and appearance of reddish-brown spots due to Fe oxidation. We observe an increase in ΔE general color change between 600 °C and 900 °C. Authors of paper [14] found that the change in the color of quartz and feldspar in sandstones occurred under heating from 750 to 900 °C. Gray GU and CG granites turn slightly into pinkish-red colors. Minerals of the black biotite group and amphibole acquire a golden-brown color on other granites, which explains a change in *b* parameter [13]. We conducted research and studied the mechanism of the change in decorative properties. The study makes it possible to determine approximately which temperature affected surface of granite by appearance of granite, and to decide on expediency of reconstruction of a building. Also, we can create fragments of facings, which should be replaced with fresh granite, based on the obtained data. The advantage of the study data is that one does not need expensive lab devices to obtain an image. However, calibration on colored standards is necessary when using common digital scanners. It is necessary to determine strength parameters of stone under heating in future. That will help to determine if facing material is suitable to perform its functions.

7. Conclusions

1. Noticeable aesthetic damage appear at temperatures from 200 to 400 °C on surfaces of natural stone samples. Thus, we can consider a fire with temperatures lower than this threshold as a “safe” fire in terms of aesthetic damage, if we take into consideration the heating coefficient of fire only and exclude ash and gases.

2. All represented granites showed a change in the color of surface at a temperature of 200 °C and above. The behavior of granites under heating depends on their mineral composition, structure and texture. Granites with red feldspar showed a progressive change in color with temperature. The largest increase in *L* component was at heating to 900 °C on samples of CG and C granites. It made up 42 and 44 %, respectively. The smallest increase in *L* component was on samples of GU and L granites under heating to 900 °C. It made up 4 and 8.5 %, respectively.

3. We observed the greatest color change on granites, where the phase transition of dark-colored minerals (biotite and pyroxene) into polymorphic minerals took place. This gave granite samples a light color, as the minerals changed color from black to gray or white. Quartz provided shades of white. White microcracks appeared under heating of quartz. The influence of temperature was less visible on red granite, since both fresh and heated samples had a similar red color. FU granite samples acquired a uniform violet-pink color at the temperature of 900 °C due to the content of apatite and fluorite. Red spots appeared on gray granites under heating. The red spots located mainly around mica and other minerals, which were rich in Fe. Reddish-brown spots appeared at the temperature of 200 °C on green VO granite. Red spots occupied 67 % of the sample area under heating to 900 °C.

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