Historical materials from the medieval fortress Bač

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Abstract

Conservation and restoration of cultural heritage are the objects of great interest worldwide. For setting the correct methodology for the procedures of the restoration it is very important to have the right information about the state of the object and the characteristics of the original materials. The basis of our examinations were clay products (samples of bricks, terracotta and clay roof tile) from the middle ages, the fortress in Bač. The following methods were used: x-ray diffraction, classic chemical analysis, SEM-EDS, Hg-porosimetry and dilatometry. Based on the used methods, mineral composition, temperature and regime of firing and textural properties of the examined materials were determined. The degree of destruction of examined materials was also identified, in order to find compatible materials for future techniques of conservation and restoration.

Keywords: degradation, clay products, porosity, mineral composition

I. Introduction

During the last two decades, architectural heritage preservation has given rise to considerable interest of scientists, architects, engineers and archaeologists. This subject is an interdisciplinary research area. When damaged, historical masonry needs to be restored with substitution bricks. A good characterrisation of both, new and old materials, gives us the possibility to forecast the chemical and physical behaviour of the new formed building system. In addition to the esthetic aspect, the familiarity with the physico-chemical properties is also a crucial parameter for maintaining the chemical equilibrium of the old materials with the adjoining ones. The historical understanding is not just to analyse the objects, but also to investigate techniques used to produce old bricks [1]. Preserved objects of cultural heritage show that bricks were the most important building material in the medieval Serbia. The technique of material manufacturing in the middle ages was simple and primitive and was an important activity in that society.

Raw materials from the close surrounding were used for constructing medieval buildings: stones from the nearby mines, sand from rivers and clays. These materials, mostly alumosilicates and silicates, were used for the production of the building elements on their original place. Shaping bricks were hand-modeled. Water was added to the clays to produce a soft plastic mix, and the material was thrown into the mould. The next step was drying for a few days and then firing for some weeks. Firing equipment was simple in the medieval Serbia. Bricks were stacked together and formed the walls of the furnace until loading. Wood was used as fuel, which indicates that the maximal temperature of firing was about 800°C [2].

Under environmental conditions bricks become unstable and suffer microstructural and mineralogical changes known as weathering or deterioration. This causes the breakdown of their minerals, allowing ionic migration and producing new mineral forms. Rock

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deterioration can be physical, via the disaggregating mechanisms of frost and salt weathering, chemical, via reactions between the mineral surface and the surrounding area (air, soil or water) or biological [3]. Biological weathering occurs concurrently with physical and chemical weathering, in fact, it can be described as physical and chemical weathering caused by biological agents [4].

The aim of this work was to study different types of building materials, to obtain information about the degree of material destruction, to define the cause of material degradation as well as the structure of the materials sampled from the historical building – Fortress of Bač.

II. Experimental

Raw materials were samples of bricks (017/07 and 019/07), terracotta and coloured film on the terracotta samples (020/07 and 021/07 respectively) and the samples of the clay roof tiles (023/07). These materials were collected from the fortress in Bač (North of Serbia, 12th centuries). Table 1 shows the position and the features of the examined materials.

The chemical composition of all samples was determined by the standard chemical analysis, while the mineralogical composition was determined by X-rays diffraction (XRD) using the Diffractometer PW 1050, PHILIPS with CuKα radiation source. Scanning electron microscopy technique with energy-dispersive of X-

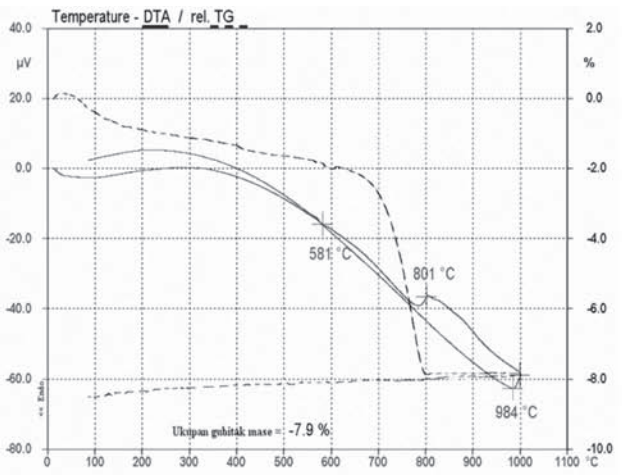
Table 1. Features and position of the examined materials in the Bač fortress

Sample	*Features*	*Position*	*Picture*
The sample of brick 017/07	Orange coloured sample covered with the layer of lima mortar	Base of the brick wall (excavated wall of the medieval palace)	
The sample of brick 019/07	Light-red-orange coloured sample	Base of the brick wall (south-east wall)	
The sample of terracotta 020/07	With-creamy coloured sample covered with light orange-brown coloured layer	Excavated pit (Buried pit under the fosters)	
The sample of clay roof tile 023/07	Red-orange coloured sample	Excavated brick wall (in-layer of the south-east brick wall)	

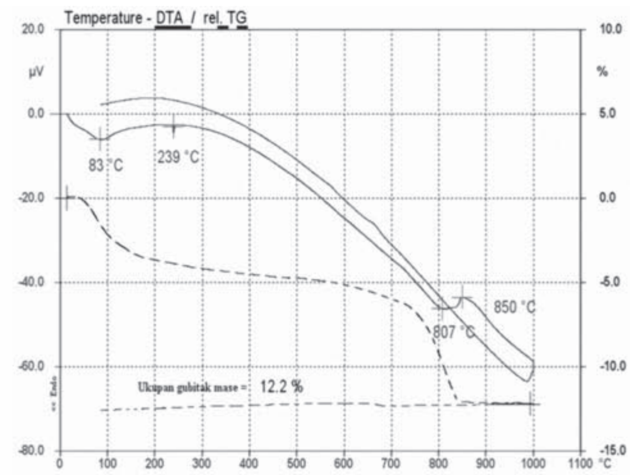
rays (JSM–6460LV, JEOL) was used for studying the morphology and the chemical composition of the defined phases. The examined samples were sputter-coated with gold, using BAL-TEC SCD 005 instrument (180s / 30mA / 50mm distance). Water absorption values of the samples were determined according to the quality standard test: European norm (EN 539–1, 1993) and American society for testing and materials method (ASTM C 373–1988). DTA measurements were recorded in the static atmospheric air, with the thermal analyser STA 503, BAHR in the range of 20 up to 1000°C, with the heating rate of 100°C/min. The samples were packed in alumina crucibles. The referent material was an empty alumina crucible. Porosity was determined by mercury intrusion porosimetry using a Porosimeter Carlo Erba 2000. Firing temperatures of the examined materials were determined on the base of Heat expansion method. The samples were refired in a Dilatometer 402E, Netzsch.

III. Results and Discussion

According to the XRD results it is confirmed that the studied samples have a similar mineralogical composition. Thus, quartz and feldspar were found in all samples. The sample of the brick (017/07) show the presence of calcite and diopside. The presence of diopside indicates the fact that the secondary calcite form was created during the processes of weathering. Thermal analysis (Fig. 1), peak at 581°C, highlights the α − β quartz structural transition. The diffractogram of the second type of brick (019/07) shows peaks which correspond to mica. The presence of mica suggests the existence of a low firing temperature of the raw material mixture since this mineral is thermally decomposed around 800°C. The XRD pattern of the sample of terracotta (020/07) shows the presence of quartz, feldspar and calcite. The existence of newly formed mineral phases such as diopside and melilite, indicates a firing temperature above 800°C [5]. A creamy-white colour of the sample of terracotta is explicable by the chemical analysis (Table 2), which shows the lack of iron oxide. The mineralogical analysis of the clay roof tile (023/07) shows similarities with the examined samples of bricks. The presence of hematite (XRD) and mass% of iron oxide (chemical analysis) explain the origin of red colour of this sample.



a)



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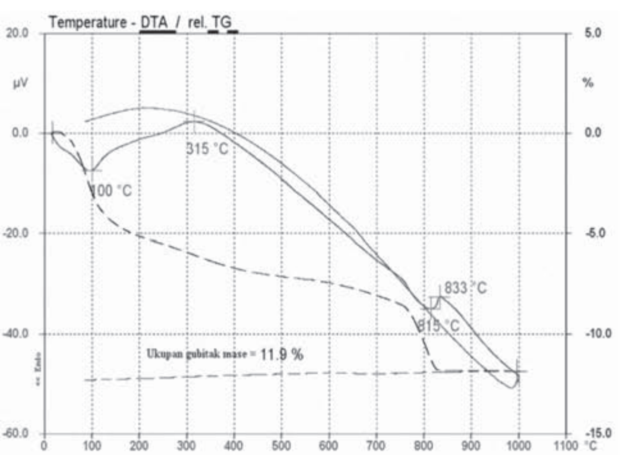
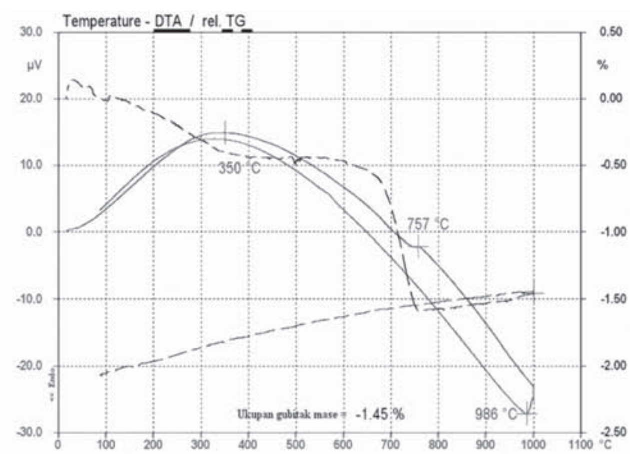


c)



d)

Figure 1. DTA diagrams of the examined samples: a) bricks 017/07, b) 019/07, c), terracotta 020/07 and d) clay roof tile 023/07

Table 2. Results of chemical analysis of the examined historical material

Oxides [mass%]	*Sample of brick 017/07*	*Sample of brick 019/07*	*Sample of terracotta 020/07*	*Sample of clay roof tile 023/07*
SiO_2	66.24	58.84	55.45	66.18
Al_2O_3	15.71	15.20	11.30	12.50
Fe_2O_3	1.44	1.35	/	4.80
CaO^*	6.59	5.30	15.42	7.51
MgO	3.91	7.36	5.56	3.30
K_2O	1.81	1.63	2.35	2.53
Na_2O	0.91	0.87	0.73	0.84
Ignitation loss*, 1000°C/2h	3.52	9.27	9.16	2.44
Total	100.13	99.82	99.97	100.10

* Difference between the results of classic chemical analysis TG /DTA and XRD is the consequence of the samples heterogenity.

The firing temperature was determined on the base of Heat expansion method (dilatometric analysis) as the point where the irreversible shrinkage of the samples occurred. The brick samples 017/07 (firing temperature 570°C in reducing atmosphere) and 019/07 (firing temperature 780°C) and the clay roof tile samples 023/07 (firing temperature 670°C) could be characterized as poorly fired. Only the terracotta samples (temperature of firing 900°C) could be characterized as highly fired product. The determination of the original firing temperature was supported by the results of XRD analysis.

Physical properties of the examined samples such as porosity and water absorption are good indicators of the conservation status of the samples, since the pores rep-

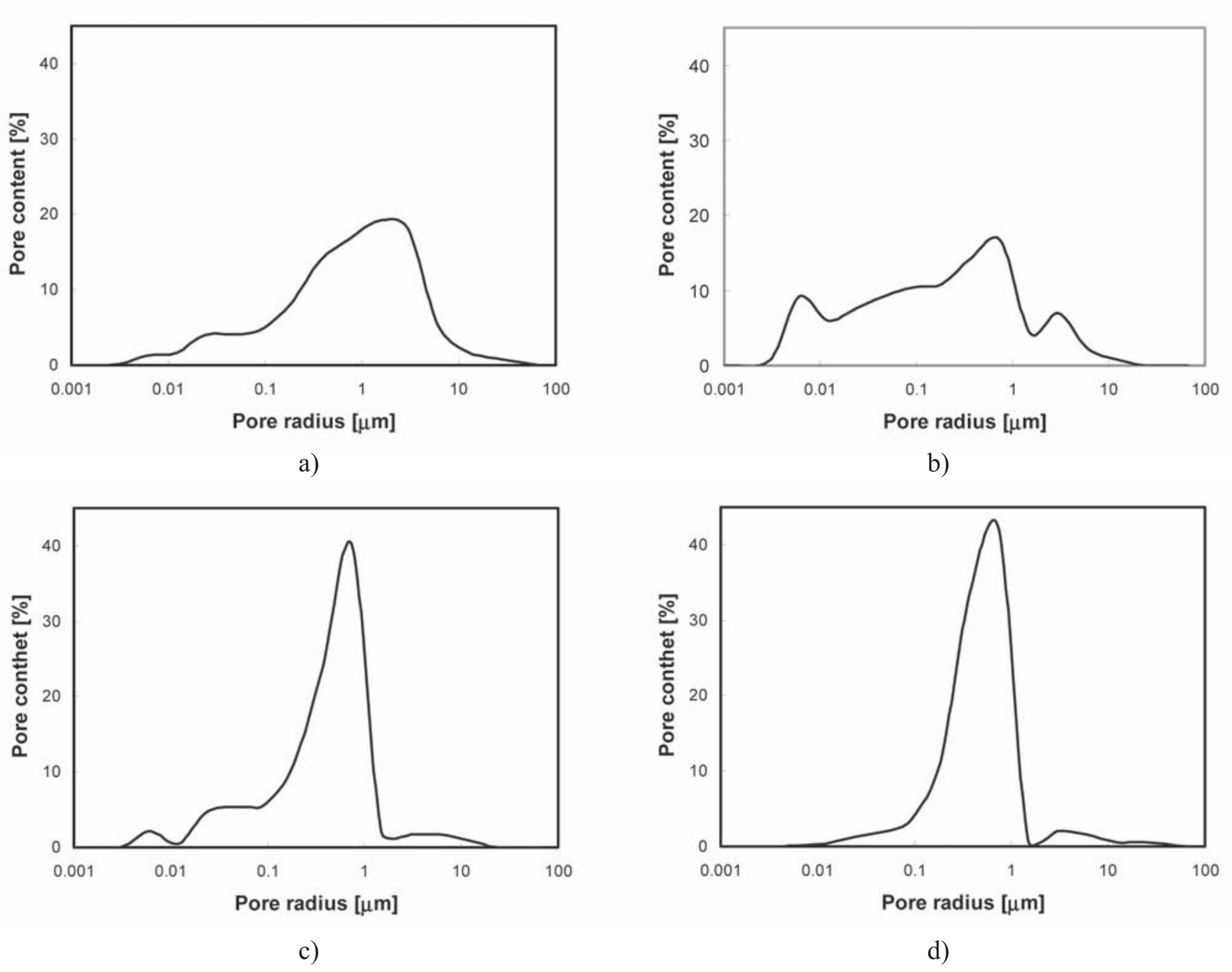


Figure 2. Pore size distribution of: a) brick 017/07, b) brick 019/07 c) terracotta 020/07 and d) clay roof tile 023/07

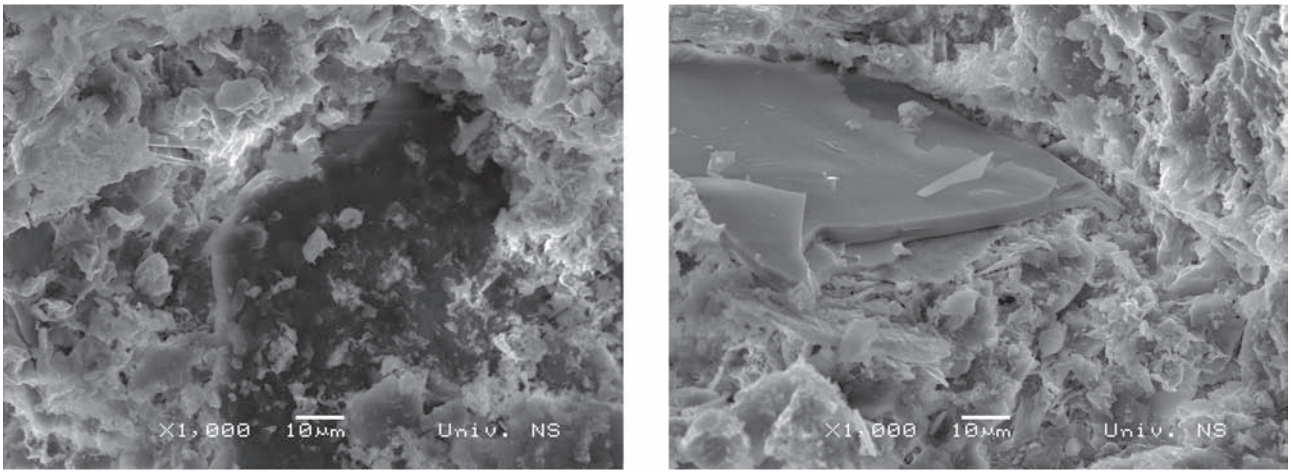


Figure 3. SEM micrographs of the sample of brick 017 / 07, × 1000

Table 3. Results of the water absorption values

Sample designation	*sample 017/07*	*sample 019/07*	*sample 020/07*	*sample 023/07*
Water absorption EU method [wt%]	18.74	16.78	25.73	20.89
Water absorption ASTM method [wt%]	22.72	18.44	27.90	21.30

resent the sites where most of the physico-chemical processes are connected with weathering. Considering the values of the water absorption of the examined samples (Table 3), the minimal value is determined for the brick samples 019/07, while the maximal one for the terracotta samples (which is caused by the firing process of the organic materials, probably straw as the component of the raw material mixture). This fact is confirmed by the thermal analysis (Fig. 1). The pore size distribution (Hg-porosimetry, Fig. 2) for all samples is similar: all have the same interval of the dominant pores, between 1 and 0.5 µm. The only noticeable difference is the portion of the dominant pores. In the case of the terracotta sample and the sample of the clay roof tile this portion is over 40 %. That is the consequence of the firing temperatures: the terracotta was fired above the decarbonisation temperature of carbonates (800°C), but below the melting point (about 1000°C) of the raw materials mixture.

The results of the SEM investigation, obtained with the magnifications from 1000× to 3000×, are shown in the Figs. 3–6. Samples of the bricks: –017/07 and 019/07; the presence of quartz grain– Q and plate of mica– M (Figs. 3 and 4) was identified. These phases are originating from the raw material mixture. Sample of terracotta is covered with the red coloured layer. Based on EDS analysis (Fig. 5) a difference between Spectrum 1 and Spectrum 2 was identified. The different amounts of manganese and iron oxide justify the char-

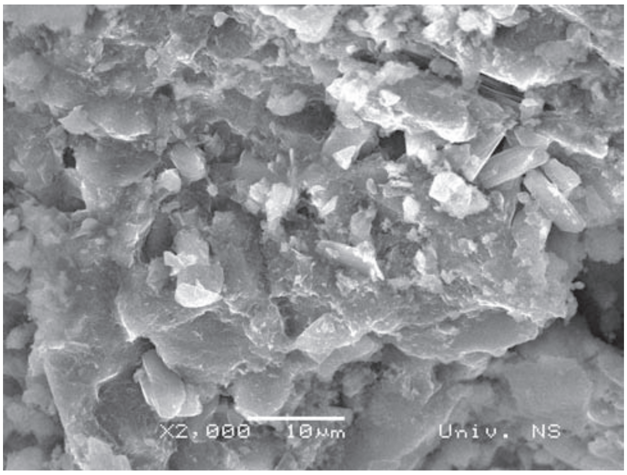


Figure 4. SEM micrograph of the sample of brick 019/07, 2000×

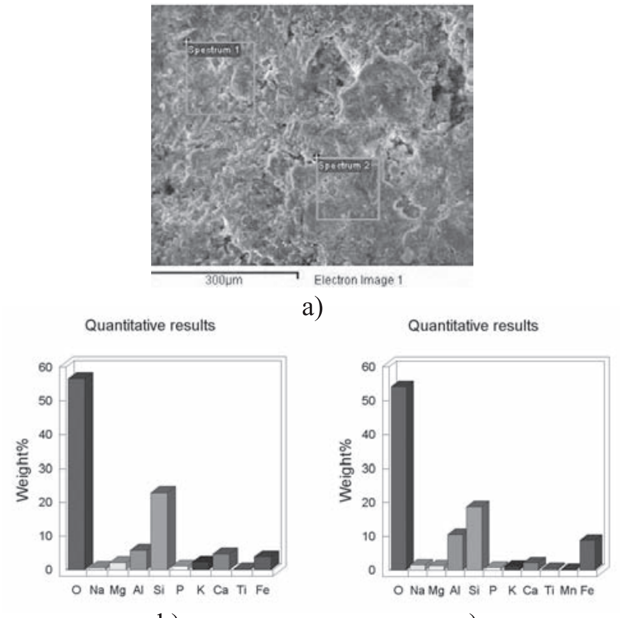


Figure 5. a) SEM micrograph of the sample of terracotta 020/07: ceramic structure (Spectrum 1) and coloured layer (Spectrum 2). EDS analysis of the sample of b) terracotta and c) coloured layer on terracotta

acterization of the red layer as a pigment – Red fired Siena. Samples of clay roof tile-023/07; the crystalline phase (Fig. 6), based on its morphology characteristics and the estimated firing temperature of 670°C (Heat expansion method), could be the mineral form known as primary anorthite.

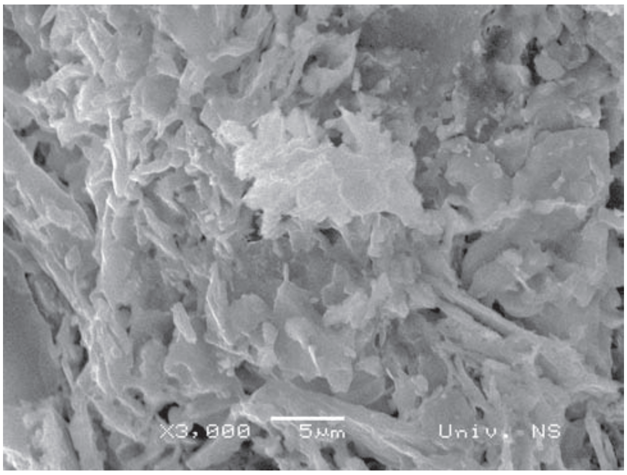


Figure 6. SEM micrograph of the sample of clay roof tile, 3000×

IV. Conclusions

The results of the examination of the historical materials from medieval fortress Bač can be summarized as follows:

Brick 017/07 is a ceramic product based on quartz, feldspar, calcite and diopside. It was fired in reducing atmosphere, at low temperature (570°C). The interval of dominant pore radius is between 0.5 and 1 μm, with a 18 vol.%. The product as a hand-modeled element, possesses a low water absorption value (18.74 mass%).

Brick 019/07 consists of newly formed crystal phase: mellilite (Ca, Na/K) (Mg,Al, Fe) (Si_2O_7) beside mineral components as quartz, feldspar and mica originating from the raw material mixture. It is a system fired at 780°C mostly in oxidative atmosphere. The interval of dominant pore radius is the same as in the case of the brick sample 017/07.

Terracotta 020/07 is a creamy-white ceramic material (mass.% Fe_2O_3 in traces and high mass% of CaO–15.47 % originating from calcite and diopside), consists of new crystal phases as mellilite and diopside. Those such as, quartz, feldspar and calcite are originating from the initial raw material. High temperature of firing (900°C) with the use of organic materials (probably straw) is a characteristic of this system. EDS analysis of the surface of the sample 020/07 (coloured layer 021/07) shows the presence of manganese, which, together with the literature data, confirms the presence of a red pigment – Red fired Siena.

Clay Roof tile 023/07 is an orange-red ceramic material (4.80 mass% Fe_2O_3), which consists of quartz, feldspar (primary anorthite form), calcite and mica as the original materials and newly formed phase as hematite. Firing temperature of 670°C was determined based on dilatometric analysis.

The data of mineral composition, original firing temperature and the textural characteristics of the historical materials are an essential background for the future production of new specific materials for the restoration of medieval fortress such as Bač.

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