# Investigation of salts souces at the Karadjordje's Gate on the Belgrade Fortress

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**Abstract**

The Karadjordje's gate is a monument of culture, part of the historical complex of the Belgrade Fortress. The gate, dated from 1740 to 1791, is made of autochthonous limestone of Miocene age. After years of exposure to environmental conditions and different anthropogenic influences, the stone blocks showed a wide range of decay forms. The gate was subject to a restoration campaign in 2007 using cement based materials. Today, the gate shows renewed signs of degradation: detachment of "artificial stone" used for restoration; scaling and disaggregation of the original stone blocks. Salts efflorescence is present around the joints of stone blocks in the upper part of the gate and under the reconstructed rosettes.
Characterization of salts was carried out by SEM-EDS and XRPD analyses. Results showed the presence of the following salts: syngenite, gypsum, thenardite, darapskite, bassanite, niter, aphthitalite and witzkeite. The paper concludes that there is an influence of restoration materials to salt contamination and to the decay of stone and "artificial stone".

Keywords: limestone, salt, restoration materials, decay

## 1. Introduction

Construction materials in monuments of culture are subject to a number of environmental factors that, acting together in different combinations, influence their degradation. Monuments are exposed to climate change, pollution, use demands, lack of maintenance, as well as inappropriate conservation treatments. Incompatibility in phisical and chemical properties of building materials, in combination with environmental factors, often causes damage of the built material.

A significant part of the damage of monuments is due to salt crystallization in the pores of stones and bricks.[1] The cristallization or hidration pressure of a particular salt or, in short „presence of salts" are often attributes of deterioration of materials.[2] The deteriorating effect of salts is grouped under the detachment category of the ICOMOS-ISCS Glossary[3] but deterioration induced by salts forms a continuum between the granular disintegration and scaling, delamination, and blistering patterns.[4] Many mechanisms are involved in the deterioration of porous materials by salts. For damage to occur, salts must move into and within porous bodies, a process that requires the presence of water or moisture.[2]

Some of main control factors of salt induced damages are: the rock fabric elements, especially porous network[5, 6], the type of salts and their amount[7], the climatic conditions, especially evaporation rate, water supply rate and mechanical resistance of the material.[8, 9]

Salts may accumulate in natural stone over time in several ways. Some of the primary sources of salt contamination include capillary uptake of ground and surface water, interaction between building materials[10], or deposition of acidity from the atmosphere.[11] Salts may also appear as a result of the interaction of aerosol pollutants with certain minerals, as in the case of gypsum[12], or may originate from mortar in contact with the stone, or even from the stone itself.[13] Other important sources of salts include biological activity[14] and polychrome, cleaning and conservation/restoration treatment.[15]

During restoration of heritage buildings, mortars are frequently used for the repointing of joints or for the "plastic" repair of stone. They consist of a binder, aggregates and sometimes additives or adjuvants.[16] Plastic repair mortars are often subdivided based on their binders, as repair mortars with cement, lime, or a combination of both.[17] Interpreting the philosophical and ethical guidelines of both the Venice Charter and the Nara Document, an ideal repair mortar for natural stone should be durable enough, but self-sacrificing on the long run.[18] Portland cement was often used in the past for repairing stone monuments. Due to the poor compatibility and low porosity of Portland cement compared to the stone types, use of this paste can have negative consequences. It forms low-permeable to the impermeable zone, which prevents circulation of moisture through the more permeable original materials and produces a accumulation of water in the more weathered original stone and to its freezing during winters.[15] The authors report that the Portland cement paste could also be a source of the water-soluble salts that contribute to the rapid disintegration of the more recently inserted slabs.

In the case of the Karađorđe's gate, on which this study was carried out, salts have emerged after the restoration treatment in which cement was used for restoration of stone blocks and joints. The study was carried out with the objective to characterize present salts and to determine their possible sources. The main hypothesis was that the cement based material used for restoration had significant influence on stone degradation that occurred after the restoration was carried out.

## 2. Site characteristics and historical background of the Karadjordje's Gate

The Karadjordje's Gate is located in the central and oldest part of the urban environment of Belgrade - the capital of Serbia. The climate in this area is temperate continental: average annual temperature 11.7 oC; average annual rainfall 669 mm/year; relative humidity 69.5% (data from the Republic Hydro-Meteorological Service of Serbia).

The gate, dated from 1740 to 1791, was not used for a long time – plans from the end of the 18th century already depict it walled up, with no bridge. It was put to use again only after World War II, during the rearrangement of Kalemegdan park and the fortress. Today, Karadjordje's gate lies in the second communication line approaching Belgrade fortress, connecting it with a part of the town along Sava River.

The gate consists of frontal (south) facade (investigated area in this paper), central aisle with two side rooms for guards and north facades built of bricks and stone. Frontal facade consists of double stone arches and it is finished with decorative cornice *(Fig. 1)*. Facade is built entirely of limestone blocks with simple decorations representing two simetrical rosettes. The gate was subject to the restoration campaign carried out in 2007. The cleaning was done by water jet and restoration of damaged stone blocks was carried out, without prior consolidation of the stone, with so called „artificial stone". Joints were restored with Portland cement mortar.

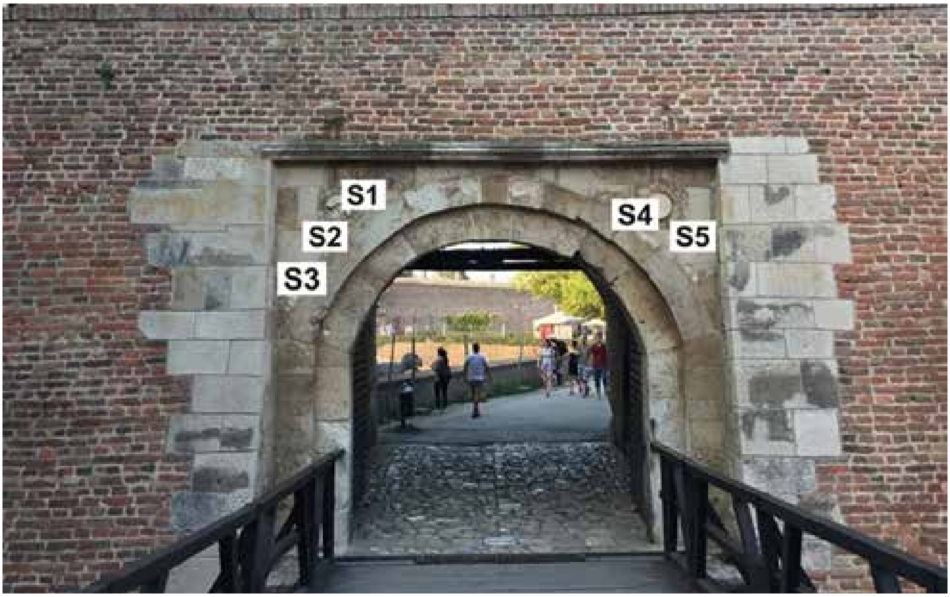


*Figure 1: The view of the Karadjordje's Gate in Belgrade (Serbia) and position of the taken salt samples*

## 3. Methodology

Salt samples were taken from stone blocks built in exterior walls of the Karadjordje's Gate in November 2016. The main criteria for the sampling positions were: significant quantities of salt in the form of efflorescence on the surface and the originality of the blocks (natural and artificial) where salts appear. In order to analyse of salt composition by X-ray powder diffraction (XRPD) and SEM/EDS, five samples of salts were taken from the substrate in following order: S1 – beneath the broken rosette made of "artificial stone"; S2 – from the surface of the cement mortar joint above restored stone block; S3 – beneath a scale on the original stone block; S4 – from contact zone between rosette of "artificial stone" and original stone substrate; S5 – beneath a scale located on the original stone block surrounded by blocks reconstructed with "artificial stone" *(Fig. 1)*.

In order to examine the built stone, structurally different samples of natural stone were taken from the monument. Petrographic analyses of the built stone were performed on thin sections using a Leica DMLSP microscope for polarised light that was connected to a Leica DC 300 digital camera. Classification of built stone was done according to textural characteristics. Determination of the weathering forms types was done according to ICOMOS-ISCS glossary on stone deterioration patterns.[3]

SEM-EDS was performed using a JEOL JSM-6610LV scanning electron microscope connected to an X-Max energy dispersive spectrometer to identify the morphology and chemical composition of the mineral phases present in the salts. The samples were covered with gold and carbon using a BALTEC-SCD-005 sputter coating device, and the results were recorded under high vacuum conditions.

X-ray diffraction analyses were used to determine the phase compositions of powdered salts and powdered limestone. The XRPD was performed using a Rigaku Smartlab diffractometer. The diffraction patterns were obtained from 4 to 70o 2θ using CuKα1,2 radiation with a scan of 5o/min.

## 4. Results

### 4.1. Characteristics of built materials

Petrographic analyses of natural stones imply that the most dominant material built into the structure are autochthonous, allochemical limestones, Miocene in age. Textural features and micro- and macro-faunal characteristics of the limestones identify them as Grainstone microfacies and Algal rudstone microfacies. These two microfacies types are limestones mineralogically composed of calcite ($CaCO_3$), with very small amounts of silici-clastic input. The limestones are whitish, pale yellow or beige in colour *(Fig. 2a)*.

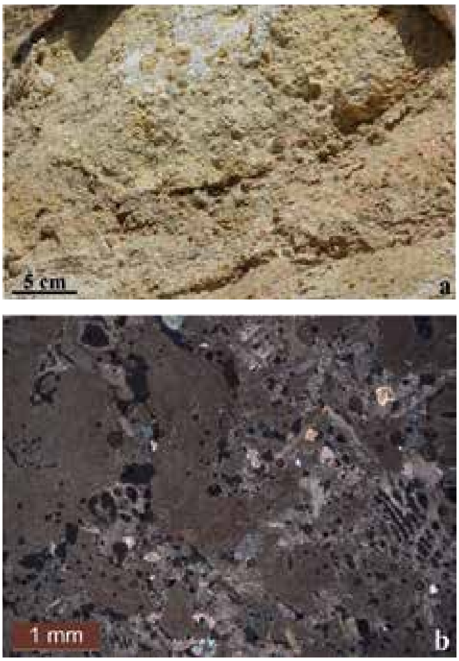


*Figure 2: The macroscopic appearance (a) and photomicrograph (XPL) of built Algal rudstone from the Karadjordje's Gate*

The prevailing allochemical compounds in all types are fossil-skeletal fragments of red algae (Lithotamnium ramisissimum; family Corallinaceae) *(Fig. 2b)*. The remains are micrite in composition with a well-developed and prominent mesh texture consisting of micron-sized rectangle chambers. Fossil remains of some other species (e.g., bryozoans, gastropods and different foraminifer species) were also recognised. They are recrystallised and filled with sparry calcite. The algal biosparrudite is extremely porous and weakly consolidated rock with sparite bounds with numerous vesicles, mesopores, rounded cavities and channels but fine/capillary pores, too. Grainstone microfacies is moderate porous rock with pores in range up to 0.1 mm. Water absorption of limestones used to build Belgrade fortress is about 15%, while the compressive strength vary from 4.5 to 13 MPa.[19]

The "artificial stone" used for restoration purposes was composed of 2 parts ground limestone aggregate, and binder that consisted of 1 part white cement and 0.1 parts slaked lime. Mineral pigments were added in order to match the colour of the original stone. Water absorption of the artificial stone was 1.6%, its compressive strength at 28 days is 43.3 MPa.[19] Portland cement mortar was used for restoration of the joints.

### 4.2. The decay forms of built stone

Mapping of the Gate's façades and registration of decay forms of stone degradation after the restoration was carried out. Damage occurs on the stone blocks at the upper part of the south façade. The most dominant decay forms are scaling and disaggregation of the original stone blocks, as well as detachment of "artificial stone" used for restoration from the rosettes *(Fig. 3a, b)*. Salts deposits occur around the joints on the stone blocks

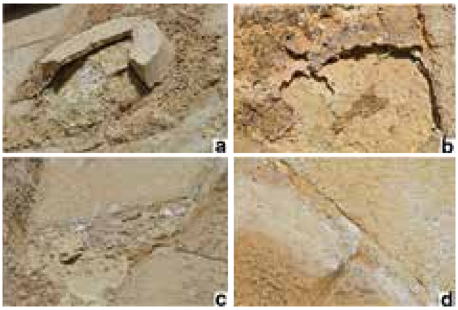


*Figure 3: The damage forms on stone blocks. a) detachment of "artificial stone"; b) scaling and disaggregation of the original stone blocks; c-d) efflorescence on mortar joints and surface of artificial stone*

in the upper part of the gate, as well as beneath the broken parts of rosette or beneath the scales on the original stone *(Fig. 3c, d)*.

## 4. Identification and distribution of present salts

XRPD and SEM-EDS analyses of the samples showed the presence of the following salts: syngenite, gypsum, thenardite, darapskite, bassanite, niter, aphthitalite and witzkeite *(Table 1, Fig. 4, 5)*.

Calcite prevails in the all samples but its presence origins of substrate. Syngenite occurs in prismatic or rarely elongated aggregates as dominant salt in all samples but vary in contents (8.5-13.4%). Gypsum in the form of tabular aggregates and variable content (4.5-20.7%) ordinarily follows syngenite in the all samples. Although thenardite is present to a lesser extent (6.5-13.4%), its presence in the form of tabular aggregates or bipyramidal crystals, is evident on the left side of the façade. Darapskite and niter (crust-like aggregates) occur up to 4% in contents. Aphthitalite occurs only in sample S1 as trigonal crystals ranging from 3 to 10 µm in content of 8.3%, whereas basanite is present on right side of outer façade (3-5%).

## 5. Conclusion

The study of damage type and salts deposits on stone blocks on the Karadjordje's gate show that there are several factors which contribute to decay of restored stone blocks as well as to the occurrence of salts. First, cement mortars used for joint filling and "artificial stone" possess different properties from the original substrate. Its incompatibility is reflected in significantly lower water absorption and greater compressive strength comparing to original limestone substrate. Orginal soft stone blocks easily absorb and release water. That indicates that the contact zone between the original porous limestone and cement mortar used for restoration represents hygric impermeable zone. Longer moisture retention

| Sample/stone type | Salt content (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | G | S | T | N | D | B | A | W |
| S1/a-o | 4 | 11 | 13 | 3 | 3 | / | 8 | 1 |
| S2/a | 11 | 9 | 7 | 4 | 1 | / | / | / |
| S3/o | 4 | 14 | 7 | 4 | 3 | / | / | / |
| S4/a-o | 21 | 11 | / | / | 2 | 3 | / | / |
| S5/o | 14 | 13 | / | / | / | 5 | / | / |

Legend: a – artificial stone; o – orginal limestone; G – gypsum; S – syngenite; T – thenardite; N – niter; D – darapskite; B – bassanite; A – aphthitalite; W – witzkeite

*Table 1: Composition of investigated salt samples*

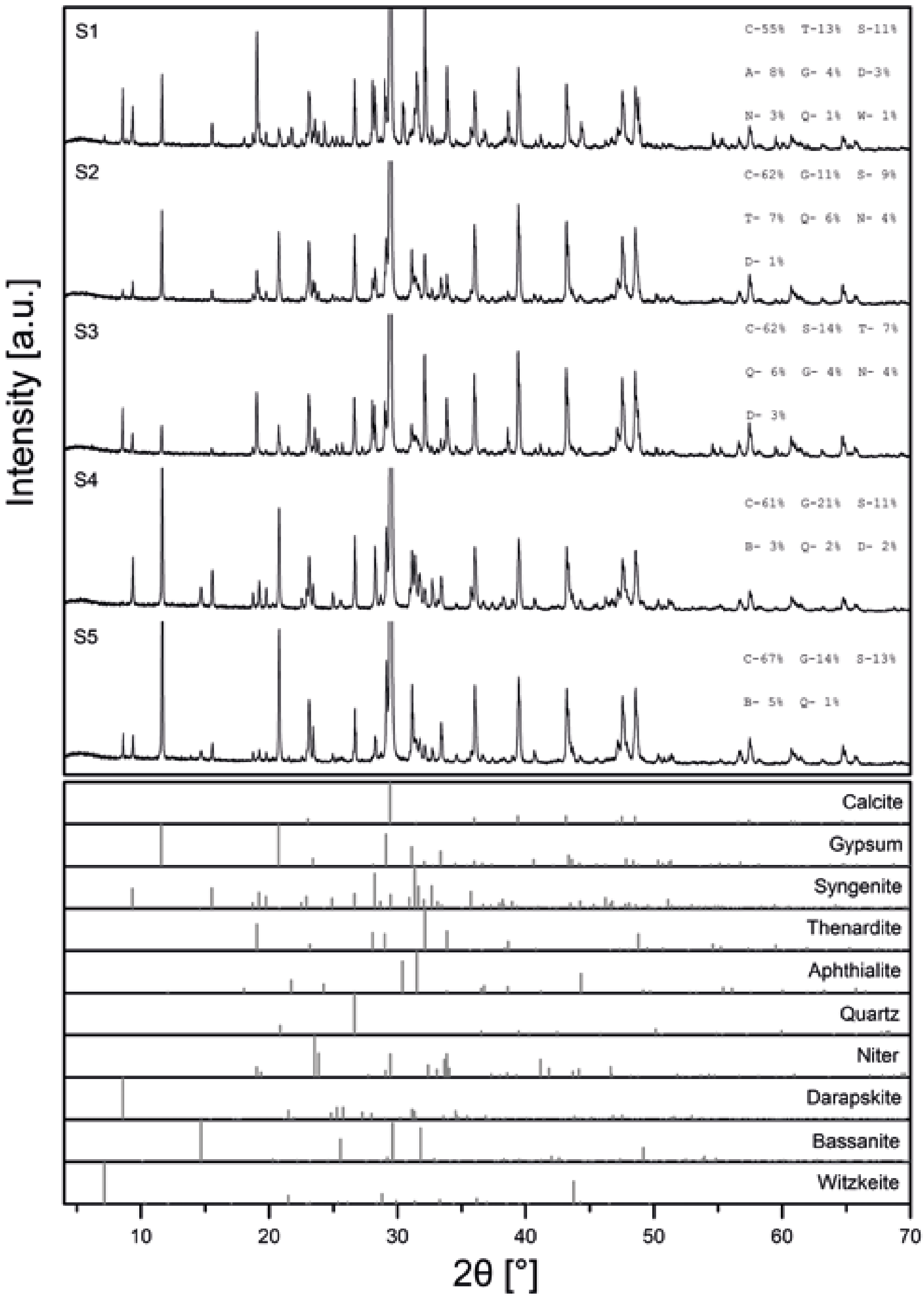


*Figure 4: X-ray diffraction patterns of the salts formed on built limestones of Karadjordje's Gate with respective semi quantitative analyses results*

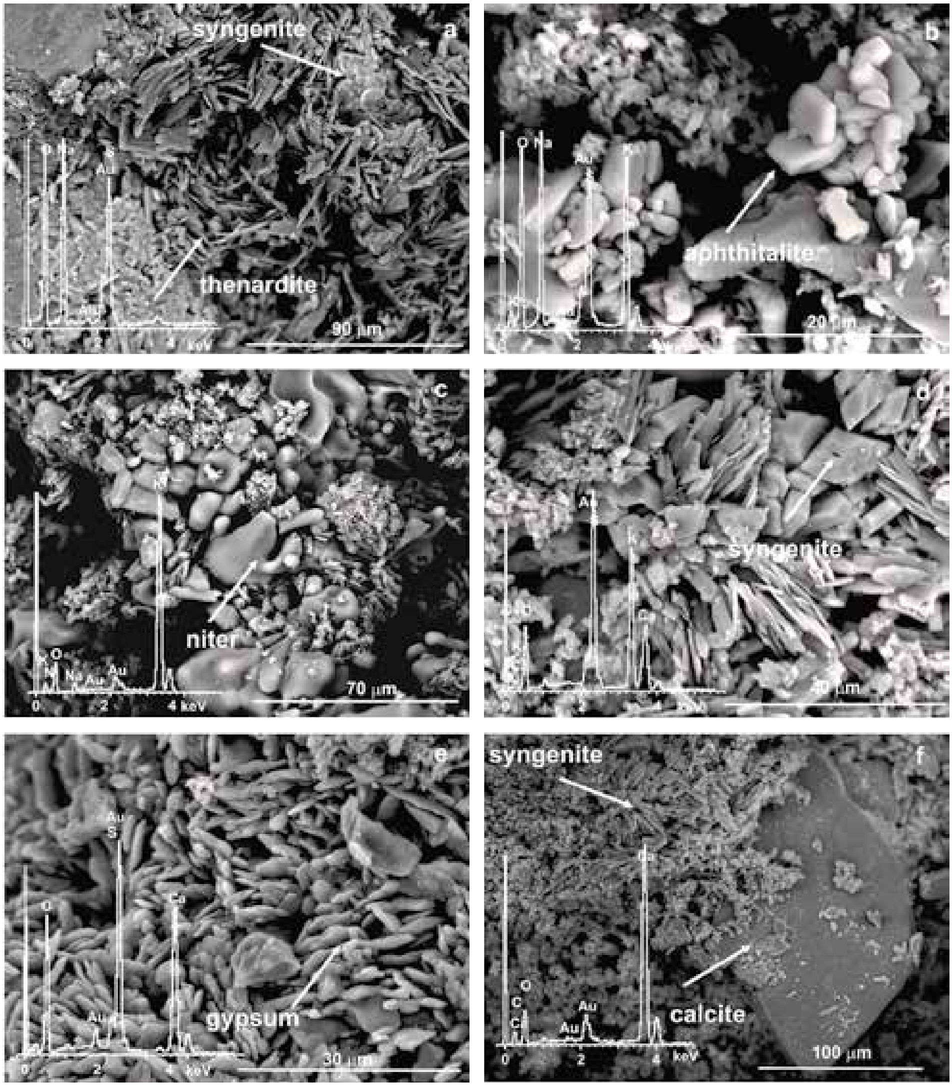


*Figure 5: SEI images with EDS spectrums of salts from the analyzed samples S1-S5*

in repair mortars can cause its chemical dissolution which could be potential source of sulphates. Water retention also causes physical damage due to freeze/ thaw cycles. Gate's architectural features and its positioning within the rampart also contribute to described degradation mechanism. Slightly indrawn south facade creates semi-sheltered area at the upper part and prevents stone blocks to be washed by rain, which is pogodna environment for the forming of gypsum. The thick earthen mound that covers the top part of the gate retains moisture which is drawn inside by capillary action and evaporates on the surface of stone blocks. The water percolation from the mound could also be the source of salts originating from grass fertilizers or decomposition of organic matter, such as niter, present in three of the samples.

This case study demonstrates the importance of compatibility of materials used in restoration with the original. If the properties of the „artificial stone" do not match those of the original, especially its hygric and mechanical properties, and if the Portland cement is used in restoration, damage is likely to occur and it will lead to the deterioration of the very stone that is meant to be protected.

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