CHARACTERISTICS OF MORTAR FROM THE ARCHEOLOGICAL SITE ROMULIANA – GAMZIGRAD

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Felix Romuliana is an archeological site located in the vicinity of Zaječar, in the east part of Serbia, south of the Danube. Felix Romuliana is a monument of Roman court architecture in the period of the Tetrachy. It is the only archeological site in Serbia, which is under the UNESCO's protection. It is a fortified palace, built at a request of the Roman Emperor Gaius Valerius Maximianus, in the honor of his mother Romula, which is why it was named Romuliana. There are two fortification systems around this palace: and older inner system, and a younger outer system which encompasses the palace, temples, military facilities, storage buildings…Mortar samples were analyzed with the goal of obtaining information about their morphological, mineralogical, chemical and basic physical properties. For an analysis of these properties, optical and scanning electron microscopy were used, as well as XRF and XRD analysis. Depending on the location of the sampled mortars, differences of the individual properties of mortar were observed. The mortar analysis determined that lime was used as a binder. The mortars prevalently consist of the river aggregate grains, crushed limestone aggregate grains and traces of crushed masonry blocks. Further research should be focused on production of repair mortars.

Keywords: *Romuliana;mortars;Stereomicroscopic;XRF;XRD;SEM/EDS*

1. Introduction

Gamzigrad (Romuliana) is an archeological site in the vicinity of Zaječar, in east Serbia, Figure 1. The archeological remains are identified as an imperial palace built at a request of Gaius Valerius Galerius Maximian, in 3rd and 4th centuries AD. The definite confirmation that these archeological remains are a palace built at the Galerius' order was finding an archivolt with a "Felix Romuliana" inscription on it, in 1984 [1]. Felix Romuliana is a place where Galerius is buried and "raised among the gods " [2]. Romuliana is included in the UNESCO cultural heritage list.

On the east side of Gamzigrad, in its immediate vicinity, runs the Crni Timok (Black Timok) river, and not far away, there is the confluence of the Crni Timok and Beli (White) Timok. These rivers represent a good source for borrowing the river aggregate used on the site. The entire area abounds in ores and most diverse types of rocks. Next to the site there is a quarry of gray amphibole, named Gamzigradit, and gray sandstone in which numerous decorations in the palace were engraved. Close to this quarry are the beds of green and pink marlstone used both as masonry blocks and for mosaics. Red limestone is excavated in the vicinity of Gamzigrad, near Krivi Vir. Coarse grained limestone, which was used for making most of the stone plastics on the site was transported from the area of the Vidrovac village, nearby the town of Negotin. In the vicinity of Gamzigrad, there are rich deposits of fine grain limestone, ranging from white, over gray to pink and red [3].

As early as by the middle of 19th century Gamzigrad was assessed as a large and extremely important archeological site. Systemic archeological research started in 1953. The excavations which ensued in the following years showed that Gamzigrad was a lavish and a showcase palace. The palace belongs to the category of monuments of Roman court architecture which is associated with the time of the Tetrarchy. The Tetrarchy was a period of division of power in the Roman Empire among four rulers. It was introduced by the emperor Diocletian.

In the course of archeological research, a large court complex enclosed by a unique defensive system was discovered. The system was comprised of a double wall formed by the remains of an older fortification. The Gamzigrad fortification system consisted of two fortification systems, a larger, younger, outer system with twenty massive, polygonal towers surrounding a smaller, older, inner system with sixteen quadrangle and octagonal towers which used to flank the gates. Previous research suggests that the building of the

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Fig. 1 - Gamzigrad (Romuliana) [Photo: A.M.Petronijević and Č. Vasić].and the Map of the archeological site Gamzigrad and regional towns.

older fortification could have commenced after Galerius' victory over the Persian king Narseh in 297 AD, while construction of the younger one began around 305 or 306 AD [1,3,4].

The research and conservation activities on the site have persisted to this day with varying intensity. Gamzigrad (Romuliana) was researched from an architectonic aspect, and analysis of gravesites and other artifacts outside the fortified area, and of other cultural layers was performed. The site was recorded using photogrammetry and considerable consideration was given to a tourist potential of the site.

Many researchers published papers about their findings from this site and the objects that were analyzed included plant and animal remains [5], usable objects made of bones, stone plastics [6], small findings, archeobotanical analyses of carbonized plant material, traces of metallurgical activities [7], silver objects, fibulae and coinage.

Brick blocks from the site were examined [8]. This paper describes the mortar from the Gamzigrad site. Due to the difference of construction times of the older and the younger fortifications, mortar was sampled from both fortifications. The possible differences in the composition and/or structure of the mortar could be the result of this time gap.

2. Experimental Procedures

Physical properties of mortar were assessed using the standard methods employed by earlier researchers to determine properties of historical mortars, including assessment of their structure and composition. In order to determine chemical composition of the mortars, a semiquantitative analysis using XRF (x-ray fluorescent spectrometry) was performed. In order to confirm the results obtained by a chemical analysis, a mineralogical analysis using XRD (x-ray diffraction), optical microscopy, scanning electron microscopy (SEM) was performed [9 – 12]. The grain and pore sizes were also assessed by optical microscopy [13, 14].

Specifically, some physical properties of mortars such as: water absorption, porosity, density and specific mass of the mortar are determined according to the provisions of the standard SRPS B.B8.032:1980. Prior to testing the volumetric mass, the samples of mortar are dried up to the constant mass at the temperature 105±5 °C. After cooling down to the temperature of 20 °C the mortar samples are saturated with water using gradual immersion method, to the constant mass, too, according to SRPS B.B8.032:1980. For determination of the volumetric mass of mortar samples, the hydrostatic balance method (KERN Germany type 572 - 49) was used. Specific mass was determined with the aid of pycnometer method (gravimetric method) [15].

For determining the elements present in the samples, the XRF analysis was performed in the Laboratory for Chemical Research, of the Institute for Mining and Metallurgy of Bor. The XRF Thermo Fisher analyzer NITON XL 3t-950 was used.

The mineralogical compounds of mortar samples were determined using XRD analysis. The samples were ground in an agate mortar before analysis. XRD method was used for determination of mineral composition of investigated samples by the GNR Explorer apparatus, with scintillating counter at a voltage of 40kV and electric current of 30mA. The intensities of diffracted CuKα radiation λ=1,540598 Å were measured at room temperatures in the steps interval of 0.02º 2θ within the range of 4º-70º 2θ and with a 2 s measuring time per step. Only crystalline species can be detected by this method and the lower detection limit is 1-3 % (w/w).

For further investigation of the composition data of the tested mortars, microscopic shots were taken using a Krüss stereo-zoom microscope fitted with a Nikon 4500 camera, and maximum magnification of 180 times for analyzed flat sections.

Preparation of the samples for SEM and SEM-EDS analysis, as well as the analysis itself were conducted in the laboratory for electronic microscopy of the University of Niš. The sample preparation process consisted in the deposition of gold in the form of a thin film on one side of the samples, in order to make the sample conducive for an electron beam. After the completed sample preparation, SEM analysis of the sample surface

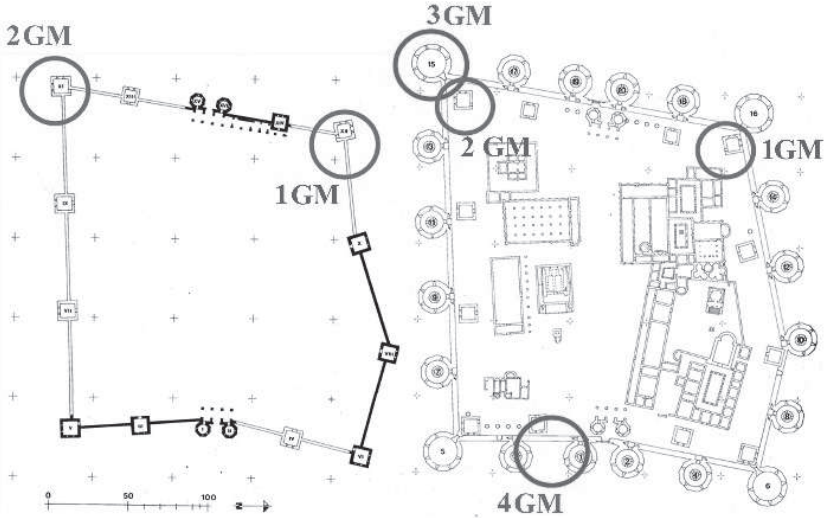

Fig. 2 - Layout of the site left-hand image: the older fortification from which the samples GM1 and GM2 were sampled; right-hand image: the younger fortification with the remains of the palace from which the samples GM3 and GM4 were sampled [4].

was accomplished by placing the samples into the scanning electronic microscope JEOL JSM-5300, which operated at the voltage of 30 kV, and the penetration depth of the electronic beam was 10 µm. After the completed observation of the sample surface, SEM-EDS analysis was conducted, The analysis was performed using the same scanning microscope, but with the detector (sensor) Linx Analytical QX 2000.

3. Sampling methods

The samples were marked from 1GM to 4GM, where GM stood as an abbreviation for Gamzigrad.

For the purpose of an unambiguous labeling of the towers on this archeological site, all the previous authors adopted a nomenclature in which the older fortification towers were labeled with Roman numerals while the towers of the younger fortification were labeled with Arabic numerals. For this reason, such nomenclature was adopted in this paper, too.

Two of a total of four samples were taken from the older fortification towers, numbers XI and XII, while the other two samples are from the younger towers (from the tower no. 15 and a part of the wall between towers 1 and 3 of the younger fortification), as seen in Figure 2.

The walls of both fortifications had the same structure. The core of the walls consisted of a rip-rap mass bound with mortar and an outer wall face made of masonry blocks. The mortar was sampled from the joints between the wall face masonry blocks.

4. Results and discussion

4.1. Physical properties of mortar: water absorption, density and specific mass

Some physical properties were tested on mortars, such as: water absorption, porosity, density and specific mass, Table 1.

Based on the values provided in table 1 it can be concluded that water absorption ranged between 21 % and 30%, porosity between 30% and 38%, density varied between 1,32 g/cm^3 and 1,61 g/cm^3, and specific mass between 2,15 g/cm^3 and 2,35 g/cm^3.

4.2. Stereomicroscopic analysis

Photographs of the samples are shown in Figures 3. As it could be observed in the photographs, the samples were relatively dense, with the clearly visible grains of the river aggregate, crushed limestone aggregate and masonry chips

Table 1

Physical properties of mortar: water absorption, density and specific mass

Sample designation	Water absorption Hm_i [%]	Porosity a_i [%]	Density g_i [g/cm^3]	Specific mass g_{si} [g/cm^3]
1GM	28.98	34.36	1.41	2.15
2GM	26.14	37.90	1.46	2.35
3GM	30.00	38.07	1.32	2.19
4GM	21.48	29.93	1.61	2.30

(this can be more clearly observed in SEM analysis, as will be displayed later). Also, presence of a binder, i.e. lime, is also visible in all photographs.

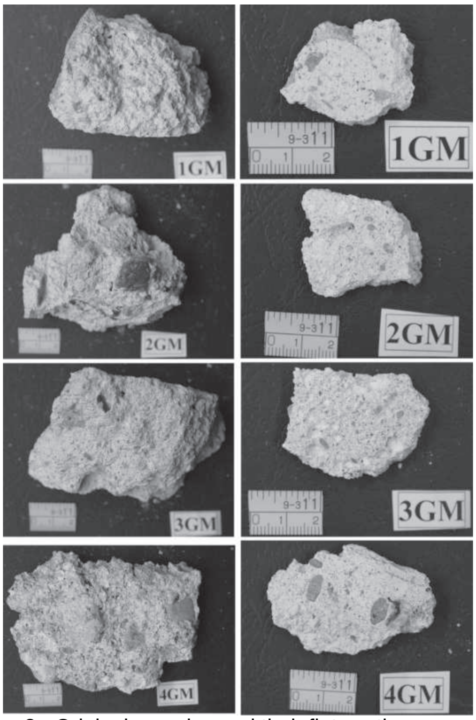

Fig. 3 - Original samples and their flat section.

Microscopic investigation of samples in Figure 4, led to a conclusion that river aggregate prevails, followed by limestone aggregate and crushed masonry blocks. There were also traces of other crushed aggregates, such as gray sandstone and marlstone.

Presence of certain types of aggregates can be observed in the Table 2. As it can be observed in the table, most of the samples feature presence of river and crushed limestone aggregate as well as brick aggregate.

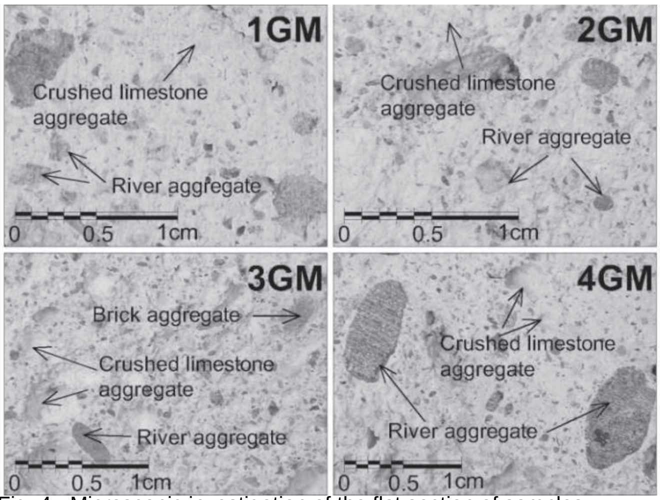

Fig. 4 - Microscopic investigation of the flat section of samples.

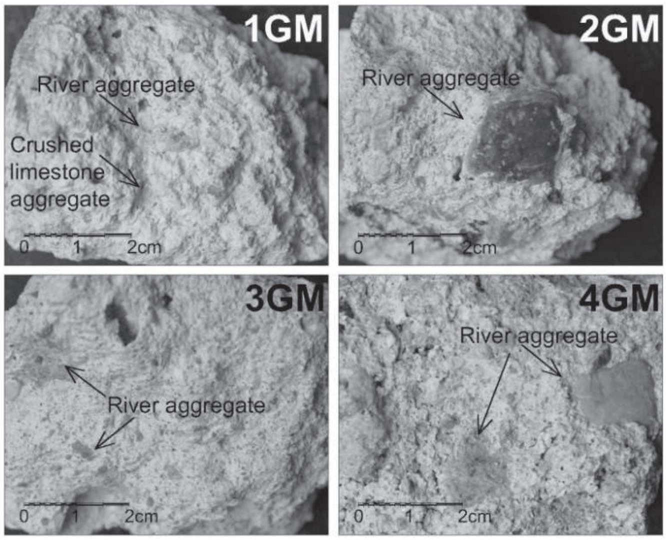

Fig. 5 - Macroscopic appearance of the sample parts used for determining aggregate grain size.

Table 2

Microscopic inspection of samples

Sample designation	River aggregate [%]	Brick aggregate [%]	Crushed limestone aggregate [%]	Cross section area [mm^2]
1GM	12.03	0.87	2.57	218
2GM	17.22	1.20	3.10	216
3GM	25.72	0.35	15.94	230
4GM	61.13	0.20	5.81	448

- % - Percent compared to the cross section area

The results in Table 3 which were obtained by a microscopic analysis of flat sections of mortar (figure 4) and macroscopic analysis of mortar sample parts (figure 5), showed that these mortars have pores and cavities (from 0,09 mm to 2,71 mm). Simultaneously, it can be seen that there is a wide range of aggregate grains diameters present.

The river aggregate featured the grains from 0,14 mm to 22,32 mm while the crushed aggregate grains range between 0,24 mm and 7,55 mm. The crushed brick aggregate can be detected only in traces so its grains dimensions were not measured.

Table 3

Grain and cavity size of samples

Sample designation	River aggregate grain size [mm]	Brick aggregate grain size [mm]	Crushed limestone aggregate grain size [mm]	Cavity size [mm]
1GM	0.96 to 9.16	trace	0.24 to 4.5	0.14 to 1.17
2GM	0.14 to 22.32	Not present	0.32 to 6.55	0.09 to 1.36
3GM	0.52 to 13.10	trace	0.56 to 3.54	0.19 to 2.71
4GM	0.57 to 13.69	Not present	0.72 to 7.55	0.20 to 2.29

Table 4

XRF semiquantitative analysis (% [w/w]) of mortar samples.

Sample designation	Na	Mg	Al	Si	K	Ca	Fe
1GM	0.60	0.53	3.96	13.11	0.88	19.82	3.38
2GM	0.80	0.43	3.97	13.30	1.00	19.20	3.79
3GM	1.20	0.78	5.07	17.08	1.04	13.05	5.51
4GM	1.09	0.88	4.97	16.71	1.08	14.54	4.80

Table 5

XRD mineralogical analysis of mortar samples

Mineral	Chemical formula	Sample number			
	Designation of samples	1GM	2GM	3GM	4GM
Quartz	SiO_2	21.5	29.4	36.4	24.5
Anorthite	$CaAl_2Si_2O_8$	8.3	22.1	25.8	25.8
Calcite	$CaCO_3$	68.6	48.5	28.8	41.1
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	1.7	-	1.7	1.8
Hornblende	$Ca_2Na(Fe,Mg)_4Ti(Al_2Si_6O_{22}(OH)_2$	-	-	3.2	5.7
Clinoclore	$(Mg_5Al)(AlSi_3)O_{10}(OH)_8$	-	-	4.0	1.1

4.3. XRF semiquantitative analysis of mortar samples

In order to determine chemical composition of the mortars, semiquantitative analysis using XRF was performed. The results are presented in Table 4.

As it can be seen in the table, the mortar samples are high in Si, i.e. in silicates (from 13,11 % to 17,08 %), then in Ca – calcium (from 13,05 % to 19,82 %) as well as in Al – aluminium (from 3,96 % to 5,07 %). Other elements are also present: Fe – iron (3,38 % to 5,51 %), Na - sodium (max. 1,20 %), K – potassium (max. 1,08 %) and Mg– magnesium (less than 1 %). Regarding the amount of Ca, it can be supposed that hydrated lime was used for the binder in mortars, while the presence of Si and Al signal indicated the prevailing usage of the river aggregate. The presence of calcium can be explained by the used crushed limestone aggregate, too.

4.4. Mineralogical analysis using XRD of mortar samples

In order to confirm the conclusions obtained on the basis of the chemical analysis, a mineralogical analysis using XRD was used. The results were presented in Table 5. The obtained results are based on the XRD spectra (Figure 6 to 9).

The obtained results indicate that the analyzed samples were high in calcite mineral (around 30 % to almost 70 %), which confirms the assumption obtained by XRF and microscopical analysis that the binder of these mortars was lime and part of the aggregate was crushed limestone. The other minerals present were quartz (around 20 %, 30 %) and anorthite (around 25 %, except in the case of the 1GM sample where it was around 8%), which indicates that in the tested mortars it was the river aggregate that was used, considering

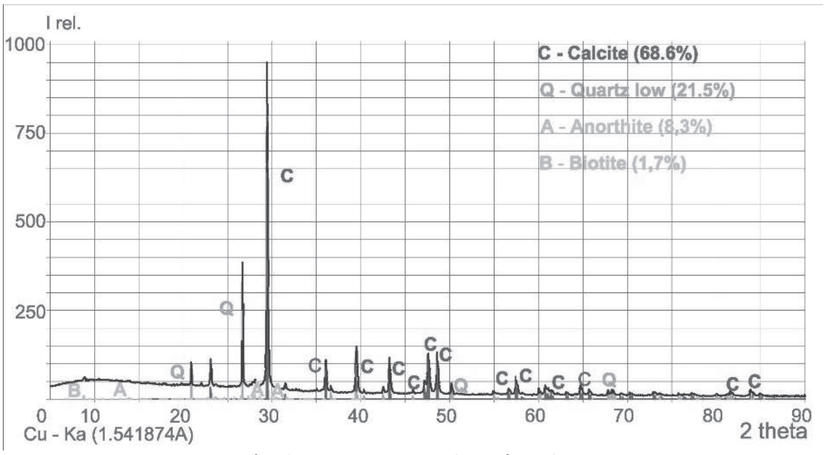

Fig. 6 - XRD pattern - Sample 1 GM.

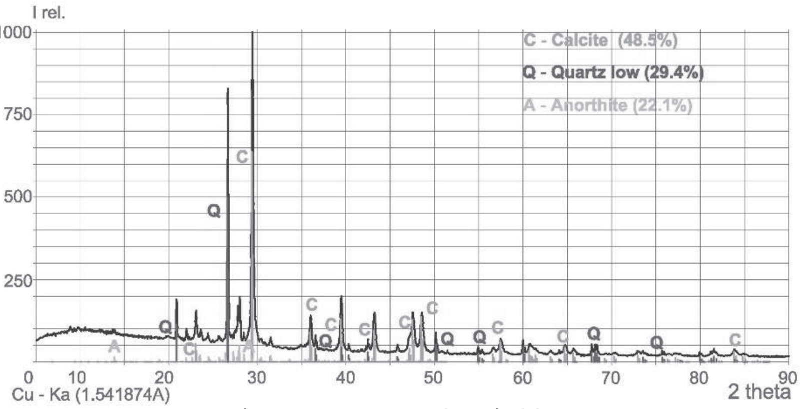

Fig. 7 - XRD pattern - Sample 2GM

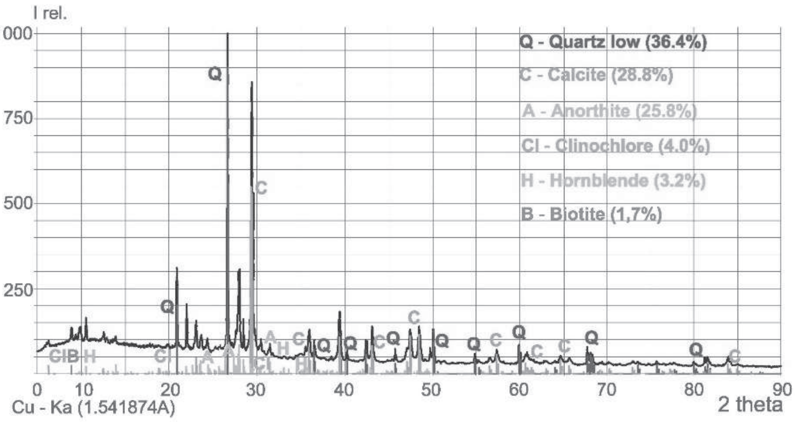

Fig. 8 - XRD pattern - Sample 3GM.

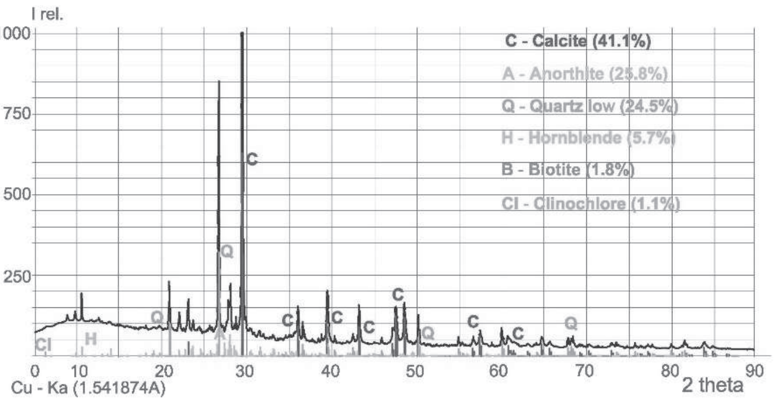

Fig. 9 - XRD pattern - Sample 4 GM.

that quartz and anorthite are characteristic for it, being classical silicate or alumo-silicate minerals. Also present are biotite, hornblende, clinoclore, to a much lower percentage than the previously mentioned ones.

4.5. SEM/EDS analysis

Some of SEM photographs and appropriate EDS spectra are shown on the Figures 10 -13.

This analysis confirmed the results obtained by XRD and XRF analyses.

As it can be seen in figure 10, the sample 1GM mostly consist of Ca and Si with some Al. This is in accordance with the XRD analysis which showed that this sample mostly consists of quartz, anorthite and calcite and the XRF analysis which indicated that the Ca, Si and Al are the main constituents of this sample.

In the case of the sample 2GM, Figure 11, EDS indicates that there is more of Si and Al in it, but also Ca is present to a considerable extent. XRF showed a similar tendency, and XRD confirms these results.

The samples 3GM, Figure 12and 4GM, Figure 13, exhibit similar SEM/EDS displays. In both samples, there is a prevalence of Si, followed by Al and Ca but there is also a lot of Fe. This especially holds for the sample 4GM. This means that in these samples, in addition to quartz, anorthite and calcite there are minerals of iron, meaning biotite and hornblende. All the mentioned statements were shown by XRD and XRF analyses. Considering the intensity of the peak of the sample 4GM it can be assumed that the recording shows that part of the sample mainly contains the iron minerals, i.e. biotite or hornblende.

This confirms the assumption that in the examined samples, the used aggregates were river aggregate, limestone with the addition of crushed brick.

5. Conclusion

Mortar samples were taken from the towers XI and XII of the old fortification, as well as from the tower 15 and the part of the rampart between towers 1 and 3 of the younger fortification. The mortars were analyzed with the goal of obtaining information about morphological, mineralogical, chemical and basic physical properties of mortar. In order to analyze these properties, XRF semiquantitative analysis, mineralogical XRD, microscopic analysis employing stereo zoom microscope, SEM/EDS analysis were used. On the basis of these tests, it was concluded that lime was used as a binder in mortars. The aggregate has a prevalently river origin. Limestone aggregate presence was low, while crushed aggregates of other kinds (gray sandstone and marlstone) were only present in traces.

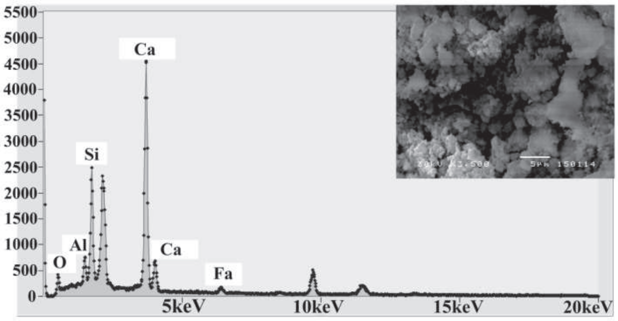

Fig. 10 - SEM and EDS - Sample 1GM.

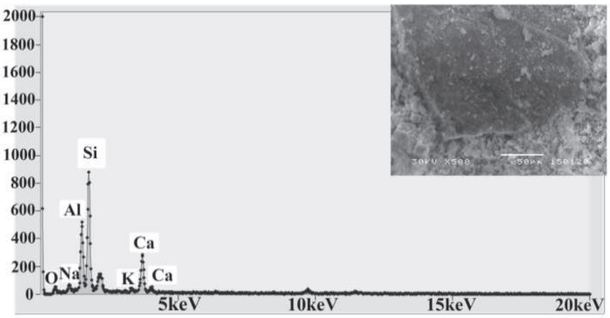

Fig. 11 - SEM and EDS - Sample 2GM.

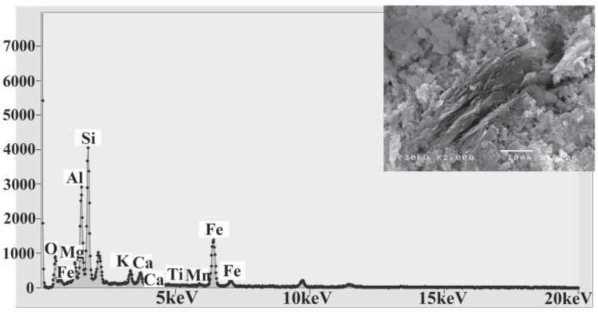

Fig. 12 - SEM and EDS - Sample 3GM.

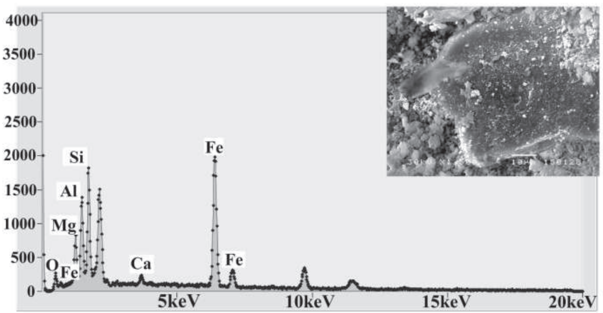

Fig. 13. SEM and EDS - Sample 4GM.

As for the physical properties and share percentage of various kinds of aggregate in the mortar samples, it is concluded that there are certain differences in the mortars from older fortification in comparison to the mortar samples from the younger fortification.

By comparing the mortar samples from the older fortification (1GM and 2GM) with the mortar samples from the younger fortification (3GM and 4GM) the following was observed:

The samples 3GM and 4GM have considerably higher share of river aggregate, and especially the sample 4GM (around 60%), in comparison to the samples1GM and 2GM (12% and 17%). On the other hand, the participation of the brick aggregate is higher in the samples 1GM and 2GM in comparison to the samples 3GM and 4GM, which belong to the younger fortification. The presence of crushed limestone aggregate is higher in the samples 3GM and 4GM (more considerably in 3GM - around 16%), in comparison to the other samples 1GM and 2GM (around 2,5 - 3%). As for the presence of cavities, no significant differences between the groups of samples were observed, which is indicated by the obtained results of porosity and water absorption (22% - 30%).

Further research should be focused on the production of repair mortars.

The first issue to be explored is the sources of the mortar components such as: limestone, river aggregate and lime as a binder. On the basis of the available components, a repair mortar most similar to the existing one should be made, and then the necessary tests should be performed.

The second option is to make the repair mortars in a combination of the existing components from the environment and new components. Caution must be exercised in using new available products so as to avoid damage of the existing structures or material. It is necessary to follow the guidelines related to the making of repair mortars which are used for historical, i.e. archeological sites. When it comes to conservation, i.e. protection of archeological sites, one should adhere to the guidelines provided by the associations and societies for protection of historical monuments, so as to preserve the existing structural status. This should be accompanied with the contemporary material research and modeling methods with a goal of producing a mortar which is as similar to the original as possible. Also, the examined mortars from the Gamzigrad (Romuliana) site should be compared to the mortars found on the archeological sites in the vicinity.

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