AN ANALYSIS OF MORTAR FROM THE ARCHEOLOGICAL SITE CARIČIN GRAD, SERBIA

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Caričin Grad is an archeological site dating back to VI century, located in the vicinity of present day Leskovac, Serbia. The city is the legacy of the famous early Byzantine Emperor Justinian I. The city, in the town planning terms, is divided into three large units. Acropolis, Middle town and Lower town, connected by the suburban area. The grandeur and importance of the city are witnessed by the remenants of several lines of city walls, planned street network, cisterns, thermae, aqueduct and sewage, numerous sacral buildings, administrative structures and housing architecture. Considering the complexity of the city, in town planning and architectonic terms, and diversity of building types in it, the mortars taken for analyses were collected from various types of buildings: from housing, public buildings, fortifications and from the aqueduct structure. In the paper, basic physical properties, as well as mineralogic, morphologic and chemical features of the sampled mortars were examined. The testing was performed using optical and scanning electron microscopy, XRF semi-quantitative analysis and XRD (x-ray diffraction). Based on the mentioned analyses, it was concluded that the main binder in the mortar was pulverized brick, which activated its pozzolanic activity. In addition, as an auxiliary binder, there was limestone powder, considering that the mortar contained the crushed limestone aggregates as well. The detected aggregate grains are the river aggregate, pieces of bricks and fine crushed limestone aggregate. These results would be further used for making the mix designs of repair mortars.

Keywords: *Caričin Grad; electron microscopy B; historical mortars; optical microscopy B; repair mortars, X-ray methods*

1. Introduction

Caričin Grad is the largest and one of the most important early Byzantine sites in Serbia. It is located next to Lebane, a town not far away from the present day city of Leskovac, in Serbia (Figure 1). The site occupies a surface area of around 70.000m^2. The urban structure of the city is composed of three entities: Acropolis, Middle town and Lower town. Acropolis is polygonal, of approximate dimensions 100/100m, and it is located on the highest and most prominent place in the city. By virtue of this, it contains the most important buildings. The Episcopal Basilica with a pond, tetraconch Baptistry, Consignatory and Episcopal palace. Lower from Acropolis is the Middle town, 230 meters wide in the north part, and 100 meters wide on its south end, around 300 m long, accommodating both sacral and secular buildings. Basilica with a crypt, basilica below the Acropolis, Cruciform church, but also Principium, villa urbana and numerous buildings of mixed housing and commercial use are all parts of this urban entity. The Lower town, apart from a large part of housing buildings in the southeast part is constituted of thermae, large cistern with the water tower, double church and the basilica with the transept. Outside the city walls are large thermae, a church known in literature as the "J" church [1-5].

Built by Justinian I during the 6th century, the city was very important. Although there is still no material evidence, most experts agree that it is Justinana Prima. It was the archbishopric and military center of the region. This archeological site has been protected by law since 1949, and has a category of exceptional importance for the Republic of Serbia, since 1979. For 12 years it has been on the tentative list of world cultural heritage [6] as a potential candidate for inclusion in the UNESCO World Heritage List.

Caričin Grad inside the city walls has been archeologically explored to a great extent, around 60% of the total surface area, with small conservation and preservation works which were performed on a third of the explored structures [1].

Research on this site has been going on since 1912, when the first archaeological excavations were carried out under the leadership of Vladimir Petković, although the site had been mentioned in the literature prior to this date. Many great names of Serbian archaeologists and architects took turns at the site: Svetozar Radoičić, Aleksandar Deroko, Đorđe Mano Zisi, Nevenka Spremo Petrović, ĐurđeBočković, ĐorđeStričević, Branislav Vulović, and others. Since 1975, the works have been taken over by Vladimir Kondić and Vladislav Popović Čedomir Vasić also greatly contributed to the research of this site. Since 1978, the research of Caričin Grad involved also the Ecole Francaise de Rome with the professors Jean Michel Spieser ansd Noel Duval of Sorbone Since 1997 the research has been headed by Vujadin Ivanišević and Bernard Bavant (France).

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Fig. 1 - Caričin Grad (Iustiniana Prima) [Foto: A. M. Petronijević]

Considering that the research has been continuing for more than 100 years, a large number of professionals in archeology, architecture, town planning and history took part in a certain way in the research. To date, a large number of papers concerning this site were published, starting from the regular reports from the excavations, to those concerning: architecture [1-4], fortification systems, town planning [7,8], then mosaics, stone plastics [9], ceramics [10], glass [11], numismatics, analysis of bone objects[12], remains of plants and animals [13]. The economy of Caričin Grada was analyzed from the archeozoological point of view [14]. Masonry blocks from this site have also been examined [15]. The visual identity of the city was analyzed through digital reconstruction. [16].

The paper analyzed the mortar samples from this site, for the purpose of determining some of their characteristics, such as chemical composition, mineralogic composition, physical characteristics etc. These data could be very useful for further research and making of repair mortars, considering that the site is yet to undergo large conservation activities.

When making repair mortars, possible sites of original mortar components in the immediate vicinity of the locality should be investigated. The possibility of using river aggregate from rivers close to the site should be considered and the matching of aggregate grains with those detected in actual mortar samples, in mineralogical and chemical terms, should be examined. The same is the case with the use of limestone, as well as crushed bricks or clay as binders. Examination of the mineralogical composition of individual components would supply the mix design of repair mortar, whose composition would be most similar to the original one. Also, plasters from the Caricin Grad site should be compared with plasters from archeological sites the same period that are located in the immediate vicinity.

Another solution would be to make repair mortar using local materials, but with the use of new components (mortars with the addition of zeolite, for example, crushed ceramic elements or some other material) [17, 18]. These materials should improve the characteristics of the repair mortar, but in such a way that it does not damage the existing structure in any way. It is very important, when making the repair mortar, to adhere to all guidelines and conditions of technical protection of the relevant competent institutions, in order to avoid damage to existing, original structures. Also, after the restoration, it is necessary to monitor the behavior of the restored materials [19].

2.Experimental section – test methods

Testing of mortar samples from this locality was performed analogous and parallel to the testing from the archeological site Felix Romuliana [13], Physico-mechanical properties were tested in the same laboratories, and same electronic microscope as well as XRF Thermo Fisher analyzer were used. The idea was to make a comparative analysis of the obtained results, which will be a topic of future papers [13].

All available methods are used for research of the historical mortar properties for as precise an assessment of structure and composition of mortars as possible. By using the mercury intrusion porosimetry it is possible to determine the pore structure [20-25], while by using optical microscopy, X-ray diffraction analysis (XRD), and SEM analysis - scanning electron microscopy [26-30], differential thermal analysis (DTA) and thermogravimetric analysis (TGA) [27,29,31,32] the composition of the tested mortar sample can be determined. In order to test the macro-porosity of historical mortars, visual procedure can be implemented by using image analysis [33] and flatbed scanners [34].

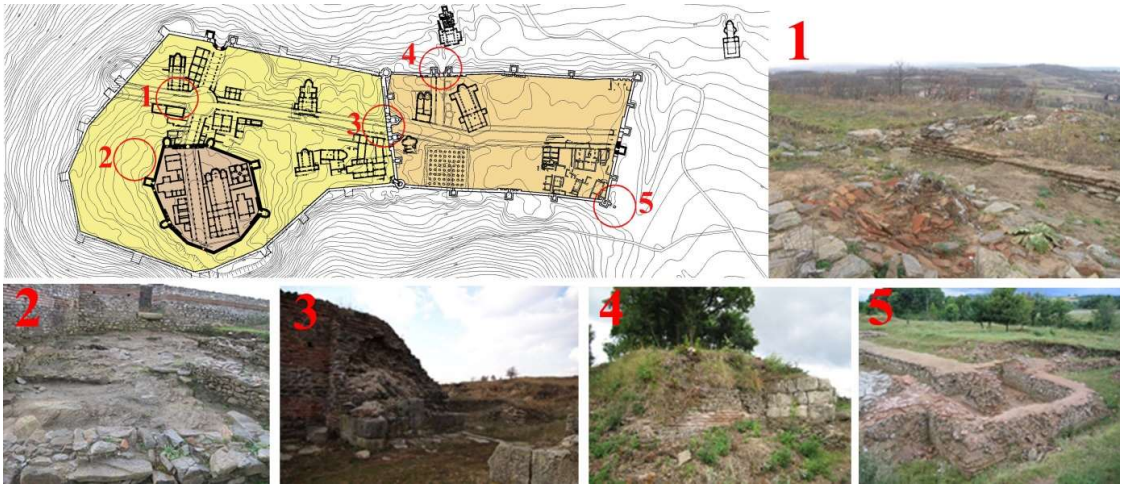

Fig. 2 - Locations where mortar was sampled on the site: buildings around the circular square of the Middle town (1) (Sample 1CG), buildings north of the Acropolis (2) (Sample 2CG), gate between the Middle and Lower town (3) (Sample 3CG), east gate of the Lower town (4) (Sample 4CG), aqueduct structure (5) (Sample 5CG). (1, 2 – photos A. M. Petronijević. 3 - 5 – photos Č.Vasić)

2.1 Samples

The mortar samples from this site were taken from different types of buildings, residential, public, fortification and aqueduct structures. From the Caričin Grad site, the mortar was sampled from the structures surrounding the circular square of the Middle town (1) (sample 1CG), from the buildings north of the Acropolis (2) (sample 2CG), from the gate between the Middle and Lower town (3) (sample 3CG), east gate of the Lower town (4) (sample 4CG), and from the aqueduct structure (5) (sample 5CG), Figure 2.

2.2 Physical properties of mortar

The following physical properties of mortars were investigated, such as: porosity and water absorption, as well as density and specific mass. The obtained results of these tests are presented in Table 1. Density and specific mass were tested according to the SRPS B.B8.032:1980 standard entitled "Testing of natural stone - Determination of bulk density, density, coefficient of density, and porosity." The mortar samples were before the density testing dried to the constant mass at a temperature of 105˚C, and then cooled to the temperature of 20˚C. In this way, mortar samples were saturated with water using the gradual immersion method to the constant mass according to SRPS B.B8.032:1980. The gravity of mortar samples was tested by the hydrostatic balance method (Hydrostatic Balance Underwater "KERN", manufacturer Germany, type 572-49) Specific mass was of the semples was determined using the gravimetric method (pycnometry method) [35].

2.3 XRF analysis

By analyzing the spectrum of fluorescent X-rays, it is possible to qualitatively and quantitatively determine the elements present. The XRF Thermo Fisher analyzer NITON XL 3t-950 was used. XRF analyses were performed in the Laboratory for chemical research, of the Institute for Mining and Metallurgy of Bor.

2.4 XRD analysis

Minerological composition of samples was determined using the XRD method. Prior to the analysis, the samples were ground. GNR Explorer apparatus, with a scintillating counter at a voltage of 40kV and electric current of 30 mA was used. The intensities of diffracted CuKα radiation of λ=1.540598 Å were measured at room temperature in interval steps of 0.02º 2θ, within the range of 4º-70º 2θ and with a 2 s measuring time per step. This method can detect only crystalline species and the detection limit wa step s 1-3 % (w/w).

2.5 Stereomicroscopic analysis

The samples of mortar were thoroughly studied using a Krüss stereo-zoom microscope fitted with a Nikon 4500 camera, and maximum magnification of 180 times.

2.6 SEM/EDS analysis

Preparation of samples for SEM and SEM-EDS analysis (scanning electronic microscopy with energy dispersive spectroscopy), as well as the analysis itself were conducted in the Laboratory for Electronic Microscopy at the University of Niš. In order to make the sample conductive for the electron beam, a thin layer of gold was deposited on one side of the sample, as a preparation.

The samples were, for the purpose of SEM analysis placed into the scanning electronic microscope JEOL JSM-5300, which was operated at a voltage of 30 kV, and the penetration depth of the electronic beam was 10 μm.

The characteristics of the sample surfaces were observed at various magnifications (x 100, x 1000, x 2000) and then photographed. SEM-EDS analysis was conducted, and it did not require further sample preparation. The analysis was performed using the same scanning microscope, but with a Linx Analytical QX 2000 detector.

3.Results and discusion

3.1 Analysis of water absorption, density and specific mass of mortar

In Table 1 are listed the mentioned physical-mechanical characteristics of mortar which were tested.

Table 1

Water absorption, density and specific mass of mortar

Sample designation	Water absorption *Hm_i [%]	Water absorption *Hm_i [%]	Density γ_i [kg/m^3]	Specific mass γ_{si} [kg/m^3]
1CG	13.80	46.68	1776	2556
2CG	17.33	57.80	1640	2588
3CG	14.70	41.42	1760	2489
4CG	15.93	51.98	1689	2567
5CG	17.67	53.0	1651	2527

** Hm_i –Ratio of water absorption to mass*
Hm = (Hmv/Hms) 100 %

As it can be seen in Table 1, water absoroption of the samples ranges between 14 and 18 %, porosity between 42% and 58%, in relation to mass; density between 1640 and 1760 kg/m^3; and specific mass between 2490 and 2590 kg/m^3. The differences in the obtained values for water absorption, porosity, density and specific mass for all five sampled mortars was observed as expected.

3.2 Stereomicroscopic analysis

The samples were labelled from 1CG to 5CG. The photographs from the number 3 to 6 present the appearance of the original samples and the photographs 7 and 8 present their flat section. As it can be seen in the photos, all the samples are fairly compact, but with clearly visible grains of the river aggregate, a large number of masonary brick chips and limestone aggregate grains are visible, but in traces (this can be seen in SEM analyses which will be presented later).

The color of the mortar samples indicates that lime was used only as randomly present binder. Pulverizing the bricks activated the pozzolanic activity, and this achieved that this powdery material was used as the main binder in the mortar. Since the mortar also contains the grains of crushed limestone aggregate,

Fig. 3 - Original samples 1CG

Fig. 4 - Original samples 2CG

Fig. 5 - Original samples 3CG

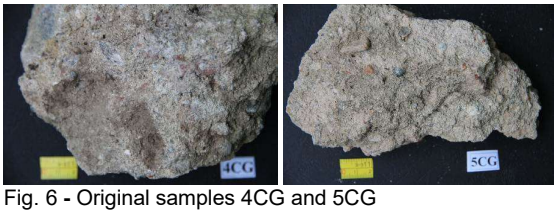

Fig. 6 - Original samples 4CG and 5CG

Fig. 7 - Appearance of 3CG and 4 CG samples flat sections

Fig. 8 - Appearance of 5CG samples flat sections

the powdery limestone was also present, so it had an auxiliary role as a binder in mortar

In order to acquire more data on the composition of the tested mortar samples, microscopic photos were taken. For this purpose stereo zoom microscope with larger magnifications was used. Magnifications ranged from x100 to x280. Some of those are the photos in Figures 9 through 12.

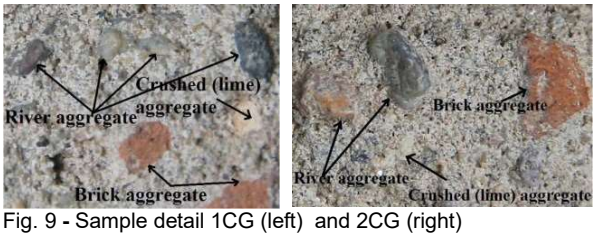

Fig. 9 - Sample detail 1CG (left) and 2CG (right)

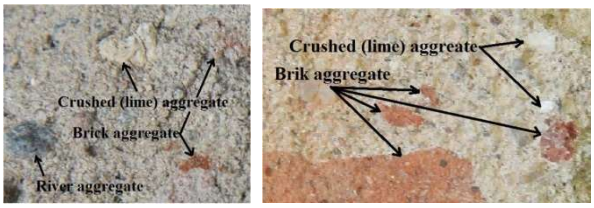

Fig. 10 - Sample detail 2CG (left) and sample flat section surface detail 3CG (right)

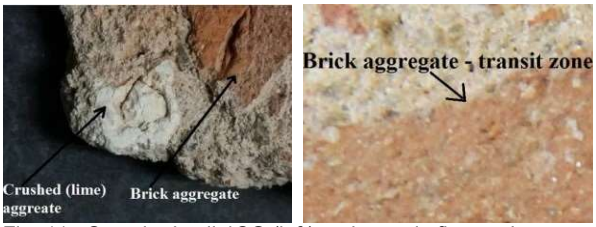

Fig. 11 - Sample detail 4CG (left) and sample flat section surface detail 4CG (right)

Fig. 12 - Sample detail 5CG (left) and sample flat section surface detail 5CG (right)

Microscopic investigation of samples in Figures 9 and 12, led to the conclusion that mortar contained river aggregate in all samples, crushed aggregate, as well as limestone aggregate. River aggregate prevailed, followed by crushed masonry blocks and limestone aggregate. There were traces of other crushed aggregates.

The photographs showed that all samples had multiple pores and cavities.

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Table 2

Grain and cavity size of samples

Sample desig-nation	River aggre-gate grain size [mm]	Brick–aggregate grain size [mm]	Crushed aggregate grain size [mm]	Cavity size [mm]
1CG	0.34 to 6.07	2.77 to 4.44	trace(0.21 to 6.72)	0.14 to 3.12
2CG	0.33 to 6.18	0.60 to 13.10	trace(0.24 to 7.07)	0.06 to 1.67
3CG	0.19 to 6.10	0.27 to 22.86	trace(0.43 to 1.39)	0.12 to 4.34
4CG	0.44 to 6.90	1.26 to 30.19	trace(0.38 to 1.73)	0.06 to 4.35
5CG	0.19 to 7.57	0.50 to 25.15	trace(0.18 to 2.22)	0.18 to 2.23

Table 2 shows the sizes of pores and cavities in various types of detected aggregate: in river, brick aggregate and crushed aggregate. The results from the Table 3 indicated that these mortars were extremely porous with numerous pores and cavities (from 0.06 mm to 4.35 mm). Also present are the aggregate grains of various sizes. The river aggregate size ranges between 0,19 to 7,57mm. Masonry chips aggregate has a grain size from 0.50 mm to 30,19mm. The crushed limestone aggregate was be present only in traces (0.18 mm to 7.07 mm).

3.3 XRF semi-quantitative analysis of mortar

For the purpose of determining the sample chemical composition, semi-quantitative analysis using XRF was performed (x-ray fluorescence spectroscopy). The results are presented in Table 3.

Table 3

XRF semiquantitative analysis of mortar samples

Sample	Na	Mg	Al_2O_3	SiO_2	K	Ca	Fe
1CG	2.77	0.43	10.00	63.80	5.65	3.11	2.25
2CG	2.04	0.54	12.00	60.50	1.23	4.81	3.66
3CG	1.43	0.69	12.90	55.20	1.81	6.00	4.49
4CG	1.51	0.52	11.70	55.10	1.17	3.93	4.50
5CG	1.48	0.49	10.10	52.20	1.00	8.90	3.63

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 24,50 % to 29,77 %), then in Ca – calcium (from 3,11 % to 8,90 %) as well as in Al – aluminium (from 5,30 % to 6,82 %). Other elements are also present: Fe – iron (2,25 % to 4,50 %), Na - sodium (max. 2,77 %), K – potassium (from 1,00-5,65 and Mg– magnesium (less than 1 %). Presence of Si and Al signal indicated the prevailing usage of the river aggregate but also the presence of crushed brick aggregate as well as pulverized brick. The presence of calcium can be explained by the used crushed limestone aggregate, too.

3.4 Mineralogical analysis using XRD of mortar samples

A mineralogical analysis using XRD (x-ray diffraction) was used, in order to confirm the assumptions obtained on the basis of the chemical analysis. Table 4 are presented the results of mineralogical analysis of mortar samples. The area scans were based on the XRD spectra, Figures 13 to 17, and the spectra themselves were recorded at the RTB Institute in Bor.

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Table 4

Mineralogical analysis using XRD (wt/wt[%]) (x-ray diffraction) of mortar samples

Mineral	**Chemical formula**	**Number of samples**				
	Designation of samples	1CG	2CG	3CG	4CG	5CG
Quartz	SiO_2	59.4	52.1	42.2	36.5	42.7
Anorthite	$CaAl_2Si_2O_8$	27.0	38.2	45.4	46.5	45.2
Calcite	$CaCO_3$	5.0	3.2	3.8	6.2	6.8
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	4.1	3.5	7.5	7.6	2.9
Hornblende	$Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$	2.5	3.0	1.2	1.5	2.5
Chlorite	$(Mg_5Al)(AlSi_3)O_{10}(OH)_8$	2.0			1.7	

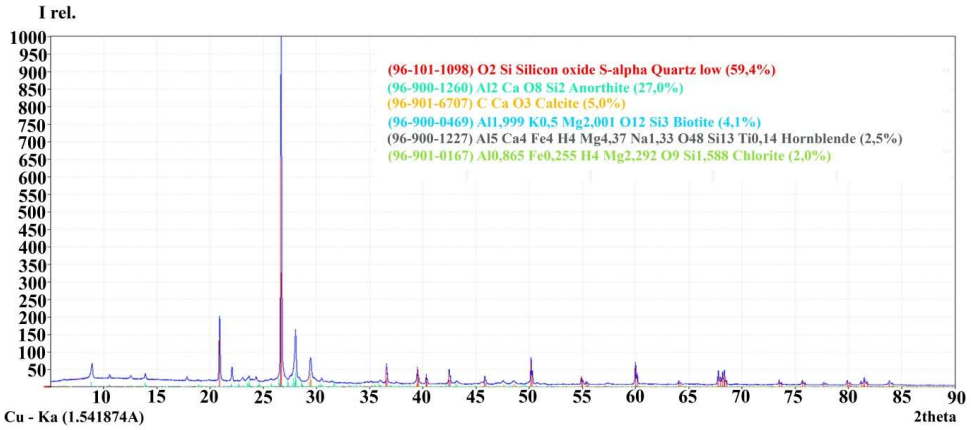

Fig. 13 - XRD spectrum 1CG

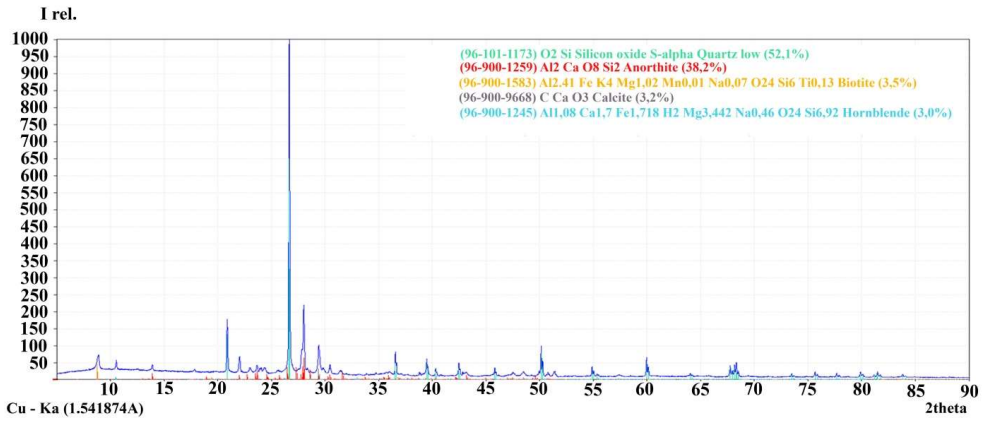

Fig. 14 - XRD spectrum 2CG

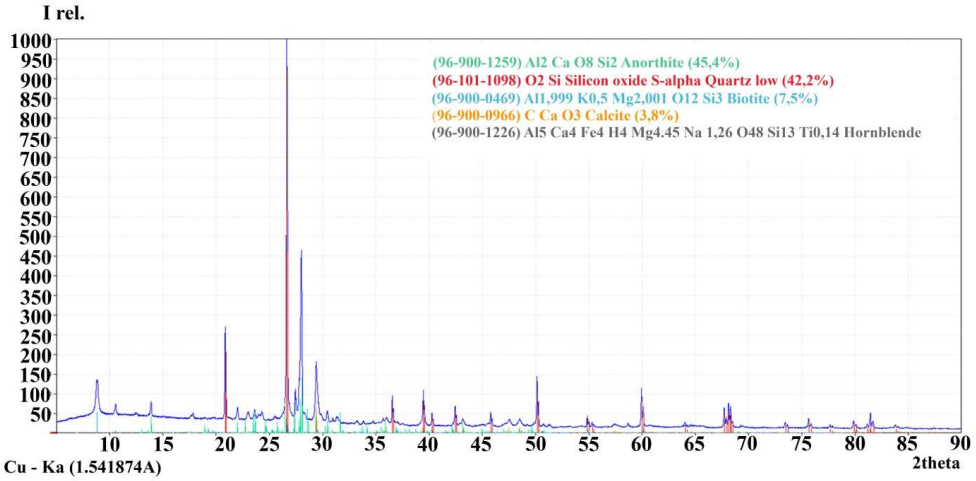

Fig. 15 - XRD spectrum 3CG

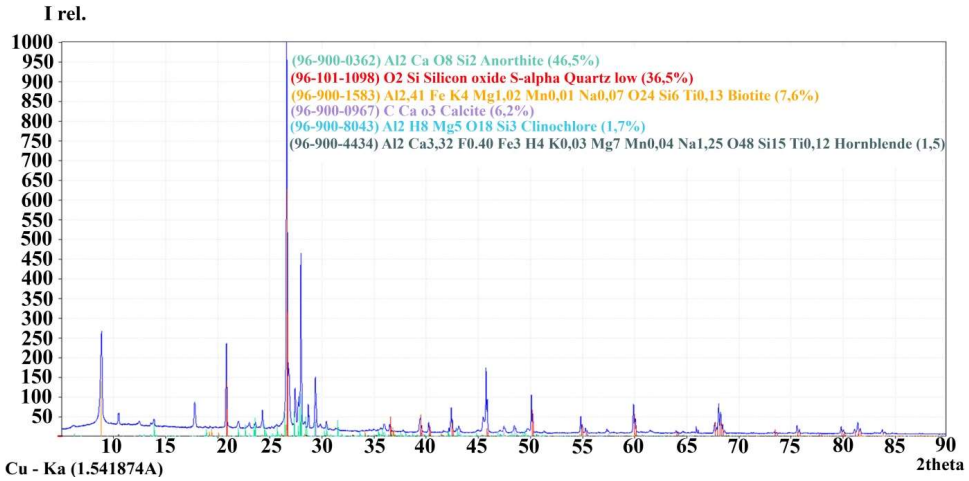

Fig. 16 - XRD spectrum 4CG

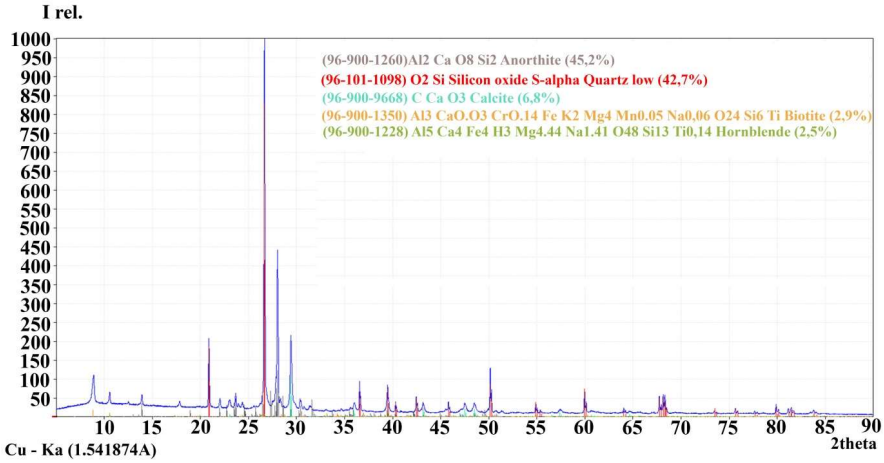

Fig. 17 - XRD spectrum 5CG

In the tested samples, apart from the prevailing quartz mineral (from 37 % to almost 60 %), there is a lot of anortite (from 27 % to 47 wt%), and a smaller quantity of calcite (4 % to 7wt%) and biotite (3% to 8 wt %). This indicates that for making of the mortar, the river aggregate was used in the most part (presence of anortite), and crushed limestone aggregate (calcite and biotite). The presence of calcite in the mentioned percentage suggests the usage of the pulverized brick as a pozzolanic material.

3.5 SEM/EDS analysis

Finally, SEM/EDS (scanning electron microscopy with energy dispersive spectroscopy) analysis was performed. In figures 18 to 22 are presented SEM photos of the samples, i.e. EDS spectra.

SEM/EDS analysis showed the same as XRD and XRF analysis. Therefore, the previously obtained results are confirmed in this way. The 1CG sample is for the most part made from Si and Al, with the presence of Ca and Fe (Figure18). This is confirmed by the XRD data showing that this sample was mainly made of quartz and anorthite with traces of calcite and biotite, i.e. together with XRF from which one can conclude that the sample consisted of oxides of Si and Al (SiO_2 and Al_2O_3) with some compounds with Ca and Fe.

In the case of the sample 2CG, in Figure19, EDS showed that on the photographed part of this sample the prevalent element was Ca with some Si and Al. Since the samples 1CG and 2CG were very similar in composition (which is showed by the XRD and XRF analyses), this means that in this case, a part of the sample consisting of some Ca mineral was photographed, indicating calcite or biotite.

The EDS spectrum of 3CG sample, (Figure20) showed approximately the same contents of Si and Al, with little Ca. It can be assumed that this SEM photograph, i.e. EDS spectrum corresponded to anorthite, considering its formula ($CaAl_2Si_2O_8$). This is in full agreement

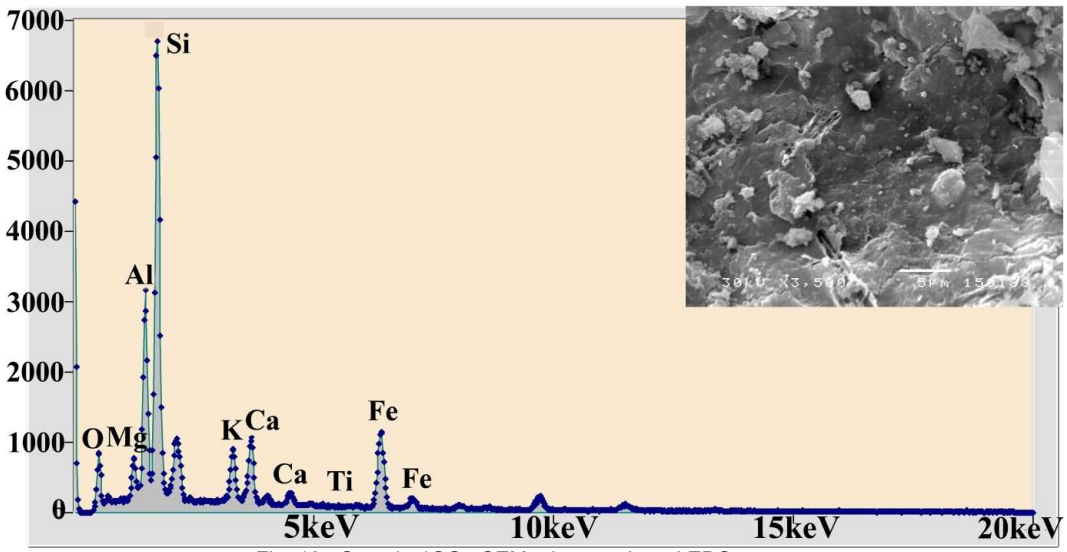

Fig. 18 - Sample 1CG - SEM micrograph and EDS spectra

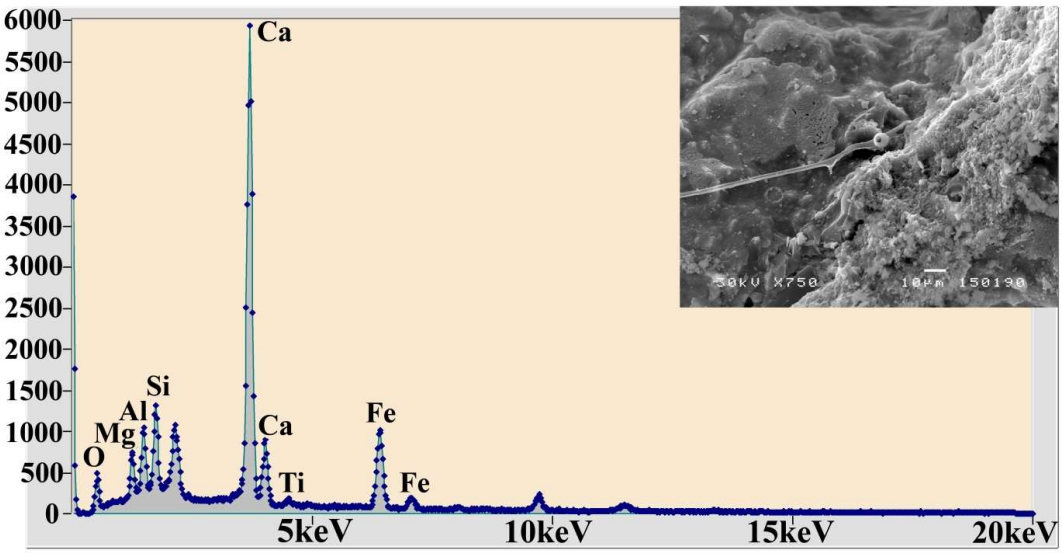

Fig. 19 - Sample 2CG - SEM micrograph and EDS spectra

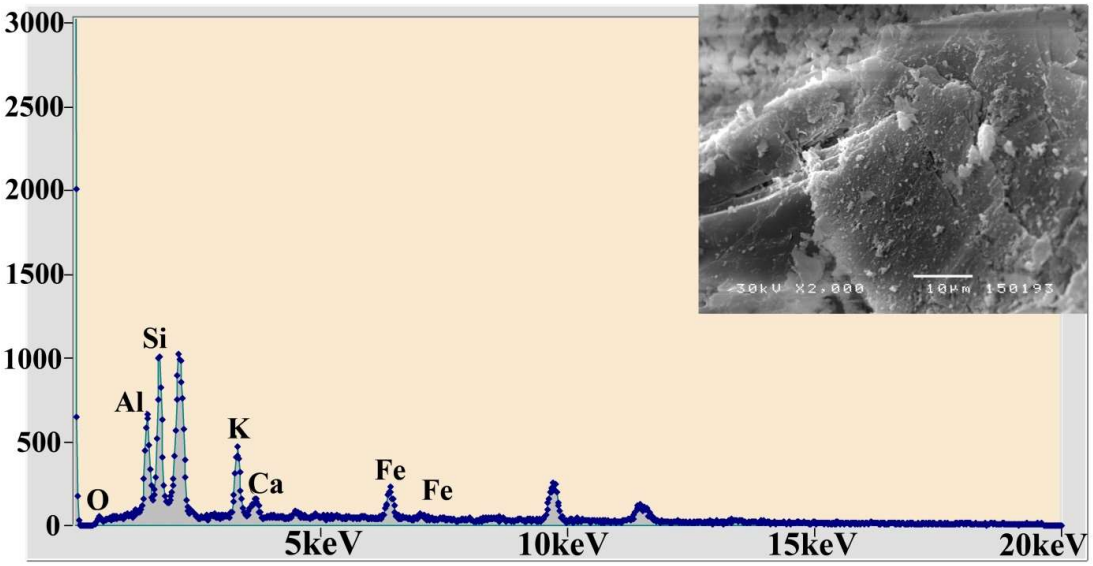

Fig. 20 - Sample 3CG - SEM micrograph and EDS spectra

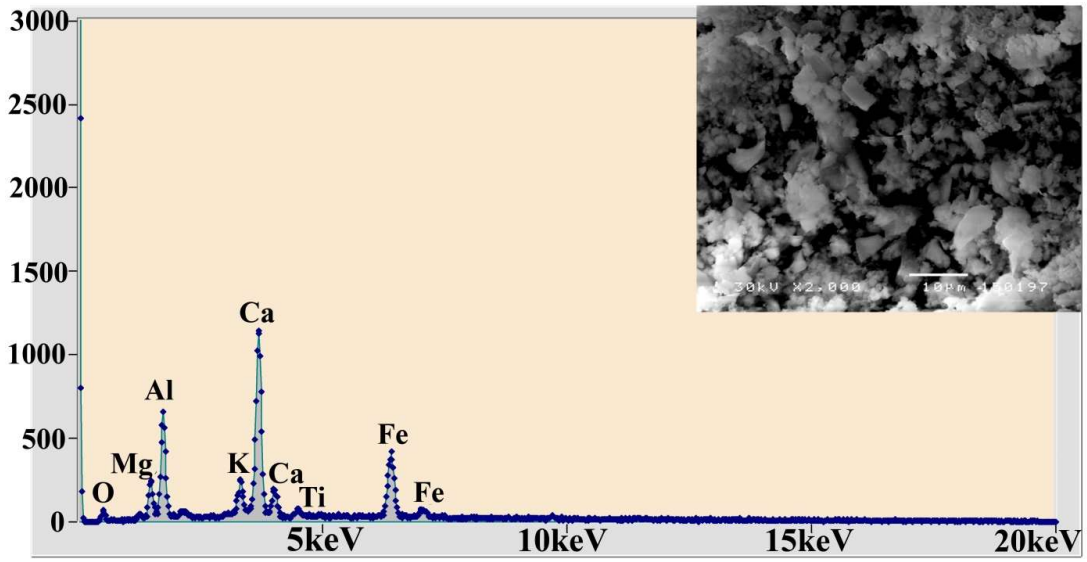

Fig. 21 - Sample 4CG - SEM micrograph and EDS spectra

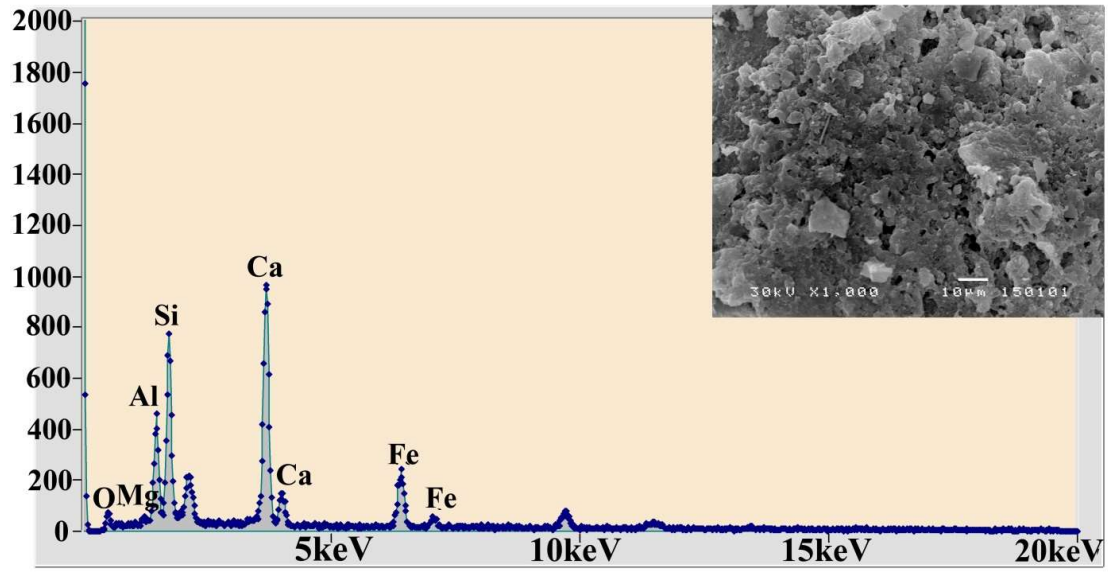

Fig. 22 - Sample 5CG - SEM micrograph and EDS spectra

with the XRD analysis which confirmed that there was over 40% of this mineral in the sample 3CG.

In the EDS spectrum of the sample 4CG, Figure 21, bands of Ca, Al and Fe were dominant. The absence of the Si band was interesting. This indicated that in the SEM photograph some Fe mineral, i.e. biotite or hornblende was which was not unexpected, because these minerals were mostly present in this sample. Finally, there is the SEM/EDS of the sample 5 CG, Figure 22. There, the EDS spectrum mostly shows bands of Si, Ca and also Al as well as the presence of Fe which is all in agreement with the obtained results of XRD and XRF analyses. All this confirms the assumption that aggregate in the samples examined was river aggregate, brick fragments and limestone crushed aggregate.

4. Conclusion

The samples of the mortar analyzed in this paper were collected from different parts of the site and from the building of various functions: sample 1CG was collected from a public building, sample 2CG was from the residential building, samples 3CG and 4CG were taken from the fortification structures, while the sample 5CG is form the aqueduct. The time when these buildings were constructed is approximately the same, 530-535 to AD, when the city was pronounced an archiepiscopal center. The mortars were analyzed with a goal of obtaining information on the morphological, mineralogical, chemical and physical properties of mortar.

Therefore, five mortar samples were sampled from five different locations in the archeological site Caričin Grad, and the following tests were performed on them: XRF semi-quantitative analysis; mineralogical analysis using XRD (x-ray diffraction); microscopic analysis using stereo zoom microscopy; SEM/EDS analysis and testing of physical properties; water absorption: porosity; and density and specific mass The main binder in the mortar was pulverized brick, which activated its pozzolanic activity. In addition, the powdery limestone occurs as an auxiliary binder, regarding that the mortar also contains the crushed limestone aggregates.. The aggregate was prevalently river aggregate. High quantities of crushed masonry blocks, a lower presence of grains of limestone aggregate, and traces of other aggregates were also detected. Regarding the physical properties examined in this paper, the values varied depending on the sampling location, as expected.

By comparing the samples, the following similarities and differences can be observed. All specimens contain an approximately the same river aggregate grain size (ranging between 0.19 and 7.57mm). The size of the brick aggregate is slightly less uniform. The 1CG specimen contains the finest crushed bricke, while the largest chips of mortar where observed in the 4CG specimen, sampled from the city fortification (30,19mm). The size crushed limestone aggregate varies between 0.18 and 7mm. In terms of the presence of cavities, it is concluded that there are no substantial differences between the specimens, which is indicated by the water absorption results (from 13.80% to 17.67%) and porosity. The mineral analysis aspect, the samples are dominated by quartz (36,5 – 59,4 %) and anortite (27-46,5 %) minerals, for the most part due to the dominant presence of the river aggregate.

Since there is almost no difference in the time when the buildings used for sampling the mortar were built, the samples have considerably uniform chemical and mineralogic compositions. As we mentioned in the introductory section, further research should deal with the making of repair mortars, and the data we presented could be very useful to this end.

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