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Characterization of Mortars from the Roman Cryptoporticus of Lisbon (Portugal)

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Abstract- The analytical characterization of mortar samples from the roman cryptoporticus of Lisbon, Portugal, was carried out by a multi-analytical archaeometric approach by means of Optical Microscopy (Stereo zoom and Petrographic microscope), Thermogravimetric analysis (TGA-DTG), X-Ray Diffraction (XRD), Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS), Acid attack and Granulometric analysis. The Roman Cryptoporticus of Lisbon, also known as the "Roman Galleries of Rua da Prata" (Lisbon, Portugal), dates from the 1st century AD. The samples were divided into six groups, according to the most abundant type of aggregates and representative characteristics. This study provides valuable data on the production techniques and the raw materials used and their possible origin. Such characterization is necessary to create compatible repair mortars as part of a sustainable conservation methodology for the future conservation plan.

Key Words:
Roman Cryptoporticus, mortars characterization, raw materials, provenance, archaeometry.

I. INTRODUCTION

The Roman Cryptoporticus of Lisbon was built in the mid-1st century AD (Silva,1934). The Roman Galleries of Rua da Prata are a chain of vaulted subterranean galleries with different heights and spans, parallel and perpendicular to each other, hidden in the downtown area of Rua da Prata, Rua da Conceição and Rua of São Julião. Like other important archaeological monuments in the city of Lisbon, the Roman Cryptoporticus was discovered after the 1755 earthquake. In 1773, the installation of the collector on Rua da Prata intercepted the building, which was immediately recognized as Roman underground monument (Moita, 1977). At the time of its discovery, the interior of the monument was already flooded due to the higher water table level present today compared to the 1st century AD. Since the discovery of the vaulted complex in 1773 to the present day, there have been several interpretations attributed to the functionality of the Cryptoporticus. The first hypothesis was a spring of water, because it was flooded when it was discovered, and the water seemed to spring naturally from the ground. And nearby there was a pedestal with an inscription dedicated to Aesculapius, the god of medicine (Moita, 1977), that currently integrates the collection of the National Museum of Archeology in Lisbon and classified as a national monument. Then it was used as a cistern during the modern period or earlier the discovery, there were also those who proposed the function as a cistern for the urbanism since its origins. Throughout time and during the 18th and 19th centuries, the initial function of the galleries has been identified by Thomaz Caetano as a baths complex (part of thermal baths) (Fabião, 1994). One of the hypotheses that unanimously agreed is the hypothesis proposed by Vasco Mantas that it might have been an architectural solution to support a construction of large buildings (usually public) in an area with a slope and little geological stability, as a result of its proximity to the Tagus River (Fabião, 1994; Mota & Martins, 2016). The current access is in the middle of Rua da Conceição, close to the tram line no 28, with steep and narrow staircase opened by the Câmara Municipal de Lisboa (CML) with the aim of facilitating visits. Currently, the galleries support two Pombaline buildings, with direct foundations resting on the vaults.

II. SAMPLING METHODOLOGY

A total of 24 mortar samples (tab.1, fig. 1) from the most representative architectural structures of the Roman Cryptoporticus of Lisbon were studied. The mortar samples correspond to different stages of excavations from different locations in the Cryptoporticus and with different

functions; 22 sample are roman, and 2 samples are from the later interventions during the 19th and 21st century (tab. 1).

Table 1. General description of the mortar samples representative of each group (G).

G	Sample	Painting layer	Location	Function	Period
1	CR-1638 CLO	No	Floor	Filling mortar	Roman
2	CR-1129A	Yes	Wall	Render mortar	Roman
3	CR-1706 M4	No	Wall	Render mortar	Roman
4	CR-915 G	No	Wall	Filling mortar	Roman
5	CR-114	No	Wall	Filling mortar	19th century
6	CR-1517	No	Floor	Filling mortar	Roman

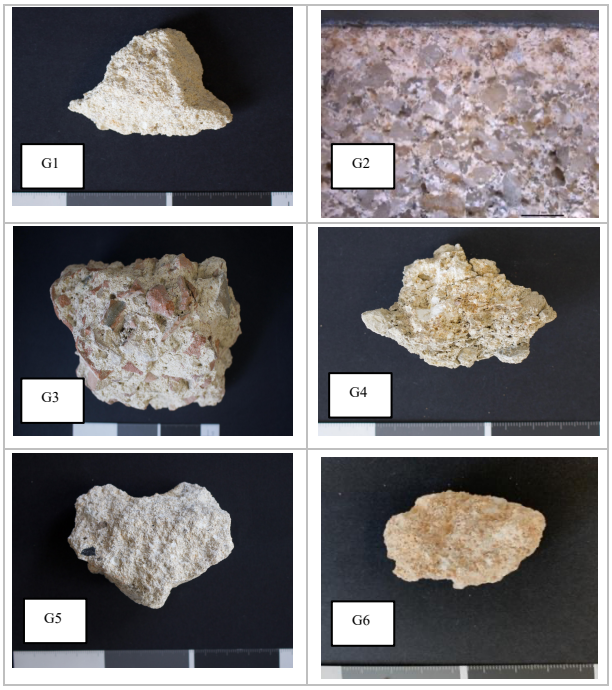

Fig. 1. Representative mortar sample from each group

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III. CHARACTERISATION METHODOLOGY

The characterization of the mortars from a textural, mineralogical and chemical point of view was carried out through the application of several complementary analytical techniques. The assessment of their characteristics was first executed by visual examination and microscopic observations through stereoscopic and petrographic microscopes.

Powder X-Ray Diffraction (XRD) was performed by X-ray diffractometer BRUKER Discovery using a CuKα source working at 40 kV and 40 mA, to gather information about the crystalline phases present in the powdered samples, which complemented the microscopic analyses.

The global fraction of each sample was used for XRD analysis and for the thermal gravimetric analysis (TGA). The TGA was performed with STA 449F3 Jupiter NETZSCH with silicon carbide furnace (RT-1550ºC), under inert atmosphere of Nitrogen with heating rate of 5ºC/min, from 40 to 1000ºC to determine the proportion of carbonates of the overall fraction of each sample.

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was used for image acquisition, elemental analysis and elemental mapping. Analysis of the samples has been performed using a Hitachi S-3700N (Hitachi High Technologies, Berlin, Germany) Scanning Electron Microscope coupled with a Bruker XFlash 5010 (Bruker Corp, Billerica, Mass. USA) with a Silicon Drift Defector (SDD) Energy Dispersive X-ray Spectrometer. SEM-EDS was used to determine the elemental composition of binder and aggregates.

For granulometric analysis, mortars were carefully disaggregated and reacted with hydrochloric acid solution (1: 3 (v/v)) to separate the fraction corresponding to siliceous aggregates from the soluble fraction.

IV. RESULTS AND DISCUSSION

A. Optical microscopy

The preliminary observation of the samples and of polished surfaces under a stereomicroscope showed that all the mortars contain sand with different proportions (fig. 2). Samples from group 1 are characterized by the presence of quartz and feldspar, in addition to a noticeable presence of shells.

As for the samples from group 2 with greenish blue chromatic layer, preparation layer and the mortar with quartz as the main aggregate. Samples of group 3 are characterized by the presence of ceramic fragments with different sizes. Samples from group 4 are characterized by the presence of angular and sub-angular limestone and sandstone fragments in the binder.

Samples from group 5, added during 19th and 21st century, are characterized by the presence of charcoal fragments as well as a small proportion of ceramic fragments and lime lumps.

The group 6 samples, mainly with quartz aggregates, are distinguished by the high presence of large lime lumps compared to the rest of the samples.

According to the macro characteristics, after studying the six groups, it can be concluded that all the groups have quartz as main aggregate that can have sub-rounded (e.g. G1) to sub-angular (e,g. G6) morphology, although there are some distinguishing characteristics of each group.

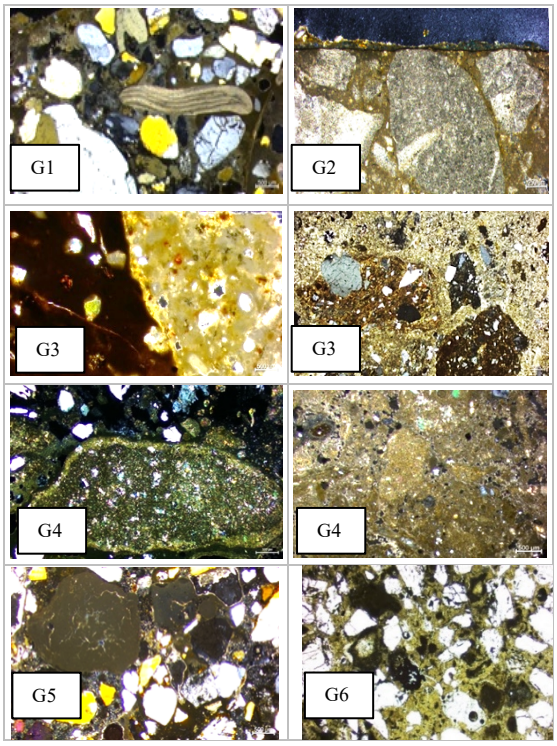

Fig 2. Petrographic features representative of defined groups. XPL (cross polarized light) and PPL (plane-polarized light). CR-1638CLO (group1), CR-1129A (group2), CR-1706-M4 (group3), CR-915G (group4), CR-114 (group5), CR-1517-4 (group6).

B. Scanning Electron Microscopy (SEM)

Eight samples have been analyzed by SEM-EDS. The presence of quartz, feldspars, and micas as aggregates, was confirmed in all samples in different amounts corroborating the result obtained by XRD and the observations carried out by optical microscopy. The presence of quartz aggregates has been confirmed by the high predominance of silicon (Si). Micas, muscovite were detected from the association of silicon (Si), aluminum (Al) and potassium (K), biotite was also detected with the addition of iron (Fe). Feldspars were identified from the association of silicon and aluminum together with either potassium (K) forming potassium feldspars or sodium (Na) forming plagioclase. In all samples, the results on binder composition are in accordance with the composition of calcitic aerial lime.

C. X-Ray Diffraction (XRD)

The XRD results show that the predominant mineral phase is quartz, which is present in all samples. Along with the quartz, all samples show an abundance in K-feldspar (orthoclase and microcline). Plagioclase felspars and micas were also obtained from powder XRD analysis in the global fraction of the sample, although in relatively lower amounts. Calcite is always present in varying amounts (tab.2). Minor or trace minerals phases identified in the samples are hematite and kaolinite.

Table 2. Mineralogical composition of the mortar samples representative of each group by XRD analysis.

G	Sample	Q	Ca	D	F		M
					Na	K	
1	CR-1638CLO	++++	+	-	+	++	-
2	CR-1129A	++++	++	-	-	++	-
3	CR-1706-M4	++++	+++	-	++	+	+++
4	CR-915G	+++	++	++	-	+	-
5	CR-114	++++	+	-	++	++	-
6	CR-1517-4	++++	+	-	-	+	-

++++, very abundant; +++, abundant; ++, present; +, small amount; -, undetected

Q: Quartz, Ca: Calcite, D: Dolomite, F: Feldspars; Na: Plagioclase, K: Orthoclase., M: Mica.

D. Grain-size distribution

Determination of the ratio between soluble fraction and insoluble residue has been performed using the results obtained by acid attack. The soluble fraction represents the binder content, soluble salts, organic matter, and carbonated aggregates while the insoluble residue constitutes of the silicious aggregates within the samples (Silva *et al.*, 2006). The percentages of the insoluble residue varied between 12% and 81% whereas the soluble fractions ranged from 19% to 88%.

The sieving of the insoluble residues allowed to determine the grain size distributions of the aggregates. The predominant grain fraction is 1.0-0.5 mm (group 1, 2, 5 and 6). Group 3 presents aggregates with higher grain size (4.0-2.0 mm) and group 4 with the smallest (0.5-0.250 mm).

According to the results obtained from the GRADISTAT statistics software samples are represented by 4 different textural groups that are gravelly sand, sand, sandy-gravel, and slightly gravelly**.** Almost all samples are poorly sorted apart group 2 which are moderately sorted (tab. 3).

Table 3. Description of the insoluble residue (Results from GRADISTAT based on Udden (1914) and Wentworth's (1922) classifications).

G	Sample	Major Fraction		Sorting	Textural Group	Mean of the agg.
		Size (mm)	Weight (%)			
1	CR-1638-CLO	1.0-0.5	35	Poorly Sorted	Gravelly Sand	Coarse Sand
2	CR-1129-A	1.0-0.5	51	Mode-rately Sorted	Sand	Coarse Sand
3	CR-1706-M4	4.0-2.0	24	Mode-rately Sorted	Sandy Gravel	Very Coarse Sand
4	CR-915-G	0.5-0.250	24	Poorly Sorted	Gravelly Sand	Medi-um Sand
5	CR-114	1.0-0.5	35	Poorly Sorted	Slightly Gravelly	Coarse Sand

6	CR-1517-4	1.0-0.5	27	Poorly Sorted	Gravelly Sand	Coarse Sand

E. Thermal analysis (TGA)

The temperature ranges were set as 40- 120°C, 120-200°C, 200-600°C and 600-900°C, where weight loss occurred. The mass losses at each temperature range were calculated from the thermogravimetric curve. The weight loss between 600 and 900ºC corresponds to the loss of CO_2 estimated as a consequence of the decomposition of calcium carbonate and thus enables the determination of the $CaCO_3$ within the samples. The $CaCO_3$ content presents a maximum percentage of 81.9% and a minimum of 6.4% (tab. 4). The simplified compositions are calculated through Jedrzejewska method using the estimated percentages of carbonates by the TGA data together with insoluble residue from acid attack (Jedrzejewska, 1960).

Table 4. Simplified compositions of the mortars determined according to the Jedrzejewska method.

G	sample	Soluble fraction (%)	Insoluble residue (%)	Carbonate (%)	Binder: aggregate
1	CR-1638-CLO	10.0	75.0	15.0	1:6
2	CR-1129-A	8.1	66.0	25.9	1:3
3	CR-1706-M4	7.6	57.4	35.0	1:2
4	CR-915-G	18.5	19.1	62.4	-
5	CR-114	25.2	68.4	6.4	1:14
6	CR-1517-4	11.1	75.0	13.9	-

V. DISCUSSION AND CONCLUSIONS

This study provided interesting information and allowed a further insight on the mortar materials and preparation techniques. Based on the results obtained by OM, XRD, TGA and SEM-EDS it was possible to determine that the use of calcitic lime, as the binding media the in mortar. In all samples, results indicate the generalized and abundant presence of Ca, interpreted as calcium carbonate ($CaCO_3$), with trace amount of Si and Al probably related with siliceous phase, such as clay. Cl and S related to the presence of salts, such as halite (NaCl) and gypsum ($CaSO_4.2H_2O$), respectively. The presence of lime lumps indicates that the lime was dry-slaked. The mineralogical composition of the aggregates is mainly quartz, feldspars and micas. The presence of Cu with Si in the pigmentation indicates that the composition might be made up of copper silicium, which might be the pigment chrysocolla based on the previous literature (Jorge, 2021). The addition of ceramic fragments to the mortar composition was found in the parts with water contact in the cryptoporticus. The most possible provenance for natural aggregates corresponds to sand deposits along the Tagus River. The more rounded quartz and feldspar grains agrees with a long distance of transportation of the aggregates, allied to the frequent presence of carbonate bioclasts and the relatively low levels of soluble salts present, the possibility that they are sediments exposed to brackish environments, of intermediate salinity, is quite plausible that this type of sedimentary deposits are located in the sediments (alluvium) of the Tagus estuary.

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