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CHARACTERIZATION OF LIME MORTARS FROM AN 18TH CENTURY RIVER TAGUS QUAY (LISBON, PORTUGAL)

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Abstract

The monumental quay Cais das Colunas was built in the decades 1770 to 1790, merged in the reconstruction plan of the city of Lisbon after the great 1755 earthquake. Characterization studies of mortars from this period are still very few. In 1997 the quay was partially dismounted and in 2008 was reconstructed. During the reconstruction intervention ancient mortars, from the core, were sampled in order to study them. This paper presents the mineralogical, chemical and granulometric characterization and capillarity water absorption of samples from these mortars. The analytical methodology comprised: the qualitative mineralogical analysis by powder method of total sample by X-Ray diffraction; the quantitative chemical analysis of total sample by X-Ray fluorescence; the water absorption by capillarity coefficient; the determination of hydrochloric acid insoluble residue; and the granulometric analysis of insoluble residue. This methodology allowed determining the simplified composition of mortars. It was confirmed the use of local sands and aerial lime based binder.

Keywords: *Historical mortars; Lisbon quay; Pombaline reconstruction; Heritage; Waterfront; XRD; XRF*

Introduction

The *Praça do Comércio* (Commerce Square) was planned and built after the great earthquake of 1755, on the site of the ancient *Terreiro do Paço* (Royal Square). The construction of the large limestone quay, built on the border of river Tagus, began in the 1770s and took nearly twenty years to complete. For more than a century, was composed by a monumental central quay flanked by two others (Fig. 1). Nowadays only the central structure remains; the *Cais das Colunas* (Quay of the Columns) which is a popular attraction for visitors to the city (Fig. 2).

Since the second decade of the nineteenth century, important persons such as royal and political personalities arrived in Lisbon via the magnificent entrance door of the *Cais das Colunas* and *Praça do Comércio*. Registered receptions include that of Princess Stephanie of Hohenzollern-Sigmaringen (1858), King Eduard VII of England (1903), King Alphonse XIII of Spain (1903), the

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Kaiser William II (1905) of Germany, and French President Emile Loubet (1905). The quay had its last glorious moment in 1957 with the reception to Queen Elizabeth II of England.

In 1910, the square including all its buildings, the King D. José equestrian statue and the quay were classified as National Heritage. The construction of a new underground tunnel necessitated the partial dismantling of the quay in 1997. It was reconstructed in 2008.

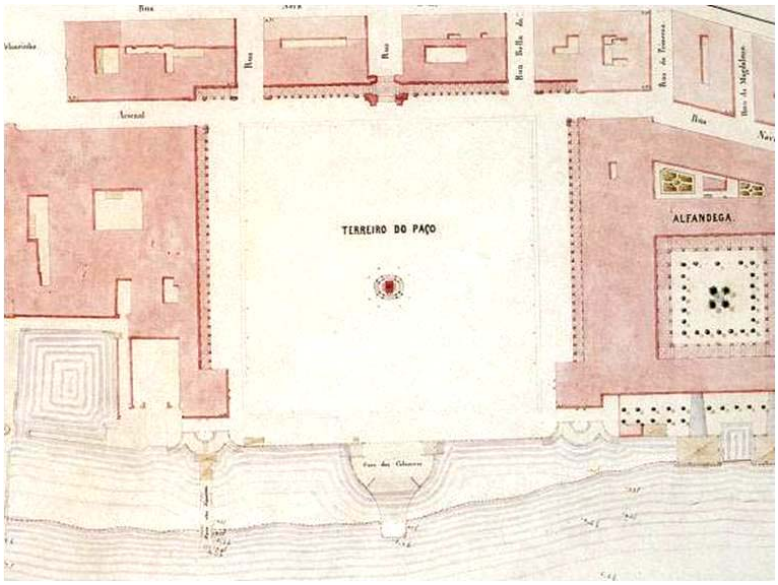

Fig. 1. Praça do Comércio (Terreiro do Paço) and Caes das Columnas, 1856-1858, by Filipe Folque. [Levantamento topográfico da cidade de Lisboa: Zona do Terreiro do Paço: N.º 51, Direcção-Geral dos Serviços Geodésicos, 1856-1858.]

Fig. 2. The quay Cais das Colunas, 2011.

The limestone quay is 50.8 metres long, its width ranging from 12.4 metres to a maximum of 44.2 metres, and is crossed by three transverse galleries. The current columns stand 6.2 metres high.

The period from 1758 until the end of the 18th century was a phase of reconstruction for the city of Lisbon, including plentiful works on maritime fortifications along the edge of the Tagus river. It is widely recognized that marine environment is responsible for specific weathering forms in historic buildings [1-3]. This determines the preparation of mortars for historic buildings, suitable for

a marine environment [4]. Since 1995, studies on the character and properties of 16th to 18th century mortars in aqueous or marine environments have been undertaken by the Portuguese National Laboratory for Civil Engineering [5-11].

During the reconstruction intervention of *Cais das Colunas* in 2008, ancient lime mortars from the core of the late 18th century quay were sampled. The aim of this research is to characterize these samples.

Materials and Methods

Samples

Sampling was carried out on the core of the quay (Fig. 3) prior to the reconstruction of western elevation in 2008. The samples collected were obtained from masonry mortars prepared and applied during the original construction of the quay from 1770 to 1790.

Fig. 3. Sampling of mortars at the core of *Cais das Colunas*. West elevation, 2008.

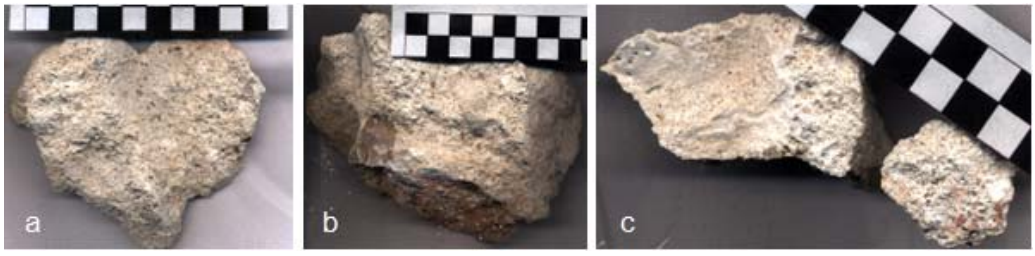

Fig. 4. Mortar samples from *Cais das Colunas*: a - MO1; b - MO2; c - MO3.

Macroscopic observation of the samples (Fig. 4) shows homogenous texture and composition. All mortars studied display high mechanical resistance.

Characterization methods

For complete characterization of the samples, mineralogical, chemical and granulometric analysis were performed as well as water absorption by capillarity coefficient tests. The methodology adopted follows published recommendations for the study and characterization of

historic mortars [12-13]. These procedures enable later execution of similar mortars for conservation works [14-19].

Prior to X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analyses, samples were dried at 60ºC, and then ground and pulverized in an agate mill. XRD allows the detection of crystalline phases present in mortars when their concentration is not very low, usually less than 3-5% [16, 20]. The amorphous components (such as soluble silicates from hydraulic pozzolanic reactions) are very difficult to detect or may be unidentifiable, so XRD results cannot be used in isolation to determine binder composition [16, 20]. XRD analysis was executed with a Philips X'Pert PW 3040/60 goniometer, using CuKa radiation, with operational conditions of 30mA and 50kV, automatic divergent notch graphite monochromator and a step size of 1º/2θ/min in the 4–65º 2θ range, with data acquisition by Philips X'Perta Data Collector v1.2. Identification of crystalline phases by XRD was carried out using the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF).

Chemical analysis by means of XRF complemented the information from XRD tests. XRF analysis was undertaken using an X-ray fluorescence spectrometer Philips PW 1410/00, using a CrKa radiation. Losses on ignition (LOI) values were obtained by heating samples at 1000ºC for 3 hours.

The water absorption by capillarity test carried out was based on the European Standard EN 15801 [21] - a method for determining the water absorption by capillarity of porous inorganic materials used for and constituting cultural property, and a quoted study on capillarity tests for ancient mortars [22]. The principle is the determination of the amount and rate at which a specimen absorbs water by capillarity through the test surface when it is in contact with water. Specimens were dried to constant mass in a ventilated oven at a temperature of 60°C. The specimens were weighed periodically at 2, 3, 4, 5, 10, 15, 20, 25, 30, 60, 120, 240 and 270 minutes.

The binder/aggregate ratio was determined by the dissolution of the mortar samples through hot hydrochloric acid attack, following a published method [23, 24]. This method is limited to mortars with siliceous sand, as acid attack dissolves calcareous aggregates thus skewing the results [13]. This method requires that the acid dissolves the binder without altering the aggregate fraction, and requires caution in interpretation as part of the aggregate fraction may not be resistant to acid attack [24].

After hot hydrochloric acid attack, the insoluble residue was washed and dried at a low temperature until constant weight was achieved. The resulting material was then sieved through normalized ASTM sieves, at meshes of 4.0, 2.0, 1.0, 0.5, 0.25, 0.125 and 0.063mm in diameter, following EN 933-1 [25], as applied in previous studies of historic mortars [26, 27]. Granulometric determination of the aggregate part inferior to 0.063 mm was performed using the sedimentation test with data acquisition by the equipment Sedigraph 5100 Micromeritics.

Hot hydrochloric acid attack and granulometric analysis of insoluble residue was limited to sample MO2, due to insufficient mortar amount of samples MO1 and MO3.

Results and discussion

Mineralogical analysis (XRD)

Mineralogical compositions obtained by XRD (Fig. 5 and Table 1) showed that the mortars from *Cais das Colunas* are mainly composed of quartz (ICDD PDF33-1161), calcite (ICDD PDF 5-586), with vestigial amounts of k-feldspar (microcline ICDD PDF 22-687) and

gypsum (ICDD PDF 33-0311). The aggregate fraction is constituted by quartz and feldspar, components originating from very mature sediments nearby. The calcite phase is the binder component formed after the carbonation process of lime. The presence of vestigial amounts of gypsum was considered to relate to the marine environment. No hydraulic phases were observed in the analyzed samples.

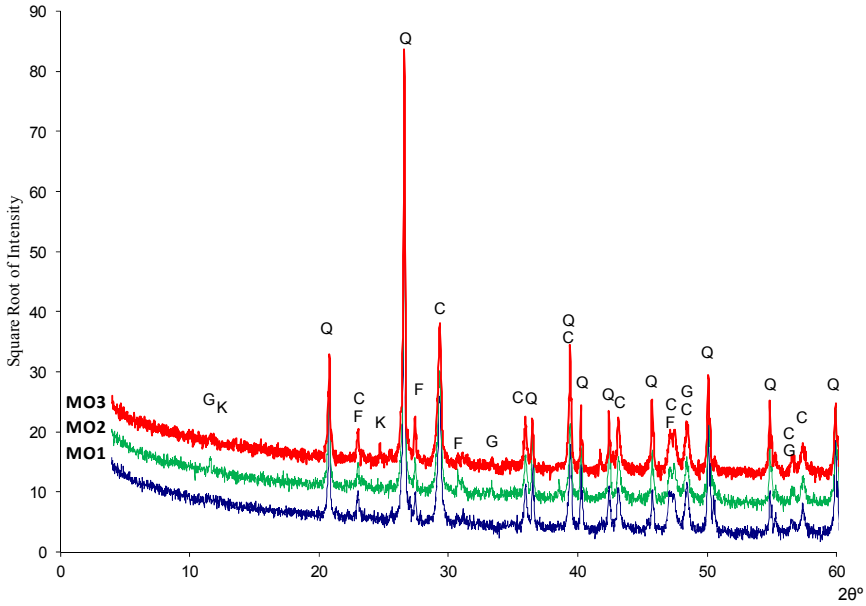

Fig. 5. Diffractograms. Q – Quartz; C – Calcite; G – Gypsum; K – Kaolinite; F – Feldspars.

Table 1. Results of XRD analysis.

Sample	quartz	calcite	feldspar	gypsum
MO1	+++	++	+	+
MO2	+++	++	+	+
MO3	+++	++	+	+

+++ high intensity

Chemical analysis (XRF)

Chemical analysis by XRF compliments the mineralogical study made by XRD. The chemical data acquired by XRF spectrometry (Table 2) shows that the main components are SiO_2 and CaO, related with quartz and calcite, as detected by XRD.

Al_2O_3 is related with the presence of K-feldspars and/or its weathering phase kaolinite [16], as seen in XRD. The minor amount of SO_3 is related with the context of the samples and appeared as a gypsum phase. The other elements do not have significant amounts that point to other minor mineral phases not detectable by XRD.

XRF results confirm that quartz and feldspar are related with the aggregate component and calcite with the binder component. Gypsum occurs as efflorescence (or neoformed gypsum), as it results from the availability of calcium ions (from the dissolution of the binder mortar) and sulfate ions (from air pollutants, as consequence of intense road traffic in the area before reconstruction works).

Table 2. Chemical composition data from X-Ray Fluorescence spectroscopy for major elements (%).

Sample	SiO_2	CaO	Al_2O_3	SO_3	Cl^-	K_2O	Na_2O	MgO	Fe_2O_3	P_2O_5	TiO_2	LOI
MO1	55.020	23.279	4.225	3.261	1.713	1.007	0.552	0.470	0.458	0.061	0.055	9.850
MO2	52.125	21.767	4.860	5.697	1.163	0.979	0.718	1.934	0.580	0.059	0.073	9.980
MO3	51.356	24.475	4.324	3.736	0.995	0.961	0.426	0.492	0.457	0.043	0.069	12.610

Water absorption by capillarity

The capillarity coefficients obtained by the contact method (Fig. 6) revealed the similarity of all samples in water absorption variation. Lower capillarity coefficient value was noted for MO3, followed by MO2 and MO1. MO1 presents the highest water absorption coefficient value. Fig. 6 presents the water mass absorbed by unity of surface versus time.

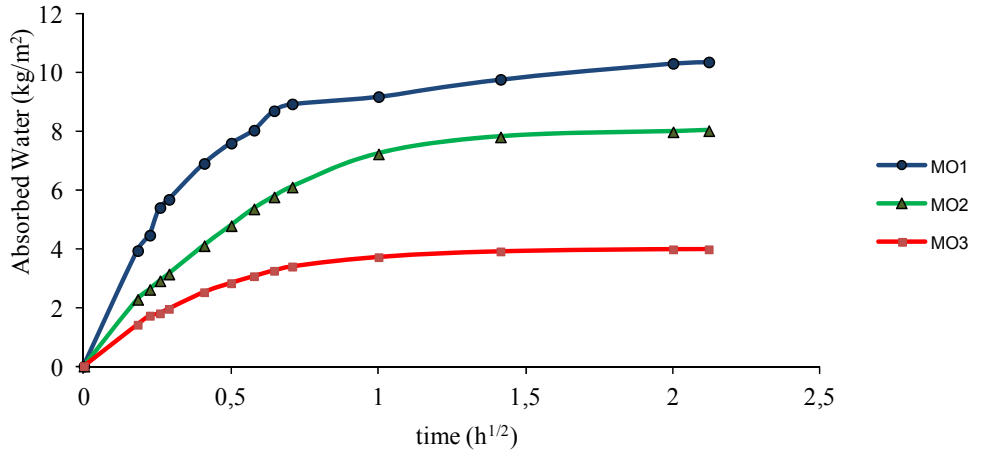

Fig. 6. Capillarity curves of of water absorption by contact.

Determination of hydrochloric acid insoluble residue

Macroscopically, all mortars show some similarity in terms of binder/aggregate ratio and in terms of particle size distribution. As mentioned only MO2 was considered.

The binder/aggregate ratio of sample MO2, in weight of dried sample, is 85%. This means, considering the specific volume for lime of 350 Kg/m^3 and for aggregates of 1400 Kg/m^3, the estimated trace binder/aggregate would have been 1:3.

Particle size distribution of insoluble residue

The particle size distribution curve and insoluble residue granulometric distribution values (Table 3 and Fig. 7) allows calculation of the grain size distribution of the aggregates. Aggregates with 0.500 to 1.000 mm diameter constitute the greatest proportion of the sample.

MO2 contained 1.53% of fine fraction, under 0.063mm. The fine particle size distribution was performed using the sedimentation process. Fineness modulus is 2.9.

Table 3. Insoluble residue granulometric distribution.

Sieve Openings (mm)	MO2 (%)
4.000	3.29
2.000	7.23
1.000	20.06
0.500	34.77
0.250	22.34
0.125	8.79
0.063	1.98
inf. 0.063	1.53

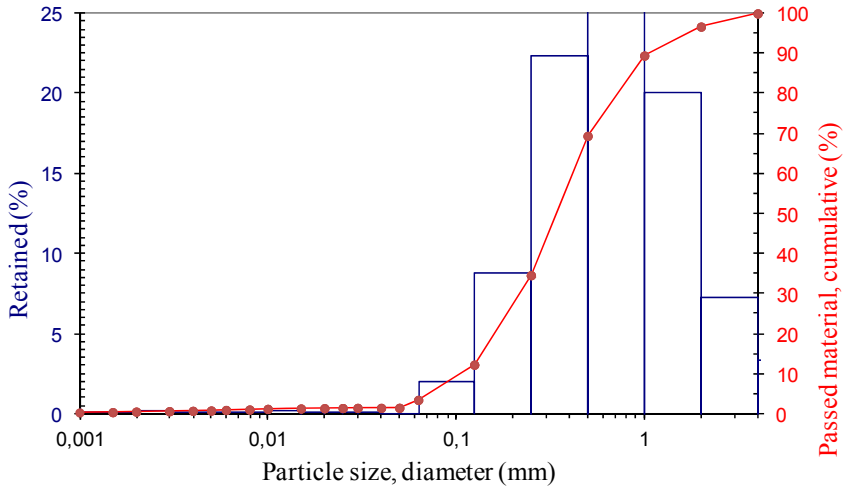

Fig. 7. Insoluble residue granulometric distribution and granulometric curve.

Conclusions

Mineralogical, chemical and textural tests were performed in order to characterize mortars samples from the 18th century quay *Cais das Colunas* on the river Tagus in Lisbon.

Mineralogical and chemically, all samples are similar indicating a traditional lime mortar with minor variations in compositions between samples. The hot hydrochloric acid attack and granulometric analysis of insoluble material indicates the estimated trace binder/aggregate would have been 1:3 with a well-washed fine sand aggregate component. The capillarity coefficient also shows behavior typical to this kind of mortars. Consequently, new mortars for any conservation works should be formulated based on the composition and texture of the original mortars, to enable successful repair works essentials for intervention in ancient structures.

Acknowledgements

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