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Characterization of Portuguese Historical Gypsum Mortars: a Comparison between Two Case Studies

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Abstract. The use of gypsum plaster for interior covering of walls and ceilings in the Portuguese architecture was particularly expressive in the period between the XVIII and the XX century. However, information about this important heritage is almost inexistent, which is leading to a fast loss of important patrimony. In this paper, the results of the characterization of gypsum plaster samples belonging to two buildings from the same historical period (end of the XIX century and beginning of the XX), situated in distant geographical regions of Portugal are presented and discussed. XRD, TGA-DTA, optical microscopy and SEM-EDS observations were used for the chemical and microstructural characterization. Some physical and mechanical properties, such as capillary absorption, dynamic elasticity modulus and compressive strength were also determined and a relationship between the characteristics observed in the samples and the technology associated to their use and application on site, as well as the possible existence of regional influences on all these aspects, are discussed.

Introduction

The importance of the preservation of cultural heritage has been particularly highlighted in the last decades. The need of sustainable interventions and the use of compatible materials are clearly supported by the last theories of conservation, namely "la Carta del Restauro de 1987" (cited in [1]), especially for buildings of historical interest.

In order to achieve the issues of compatibility, a complete characterization of the original materials is required and assumes an extremely important role in the design of the new repair products. The gypsum plaster materials are not an exception. The characterization work of the Portuguese historic gypsum plasters has never been done and lack of efficient solutions for their preservation is leading to a fast loss of important patrimony. This is the lacuna that one aims to reduce with this research study of which the two case studies presented in this paper are a part.

Experimental Programme

Case studies. The samples studied in this paper were extracted from two contemporary buildings, localized approximately 400 km away:

Estoi Palace. Situated in the village of Estoi, district of Faro, *south* of Portugal. Its construction started in the middle of the XIX century but it was only finished between 1893 and 1909, with the decoration of the house and gardens. The decorative program was conceived by Domingos Meira, an architect and decorator responsible for other valuable plaster works in Portugal and results from a mix of architectonic styles, where Neoclassic, Neorocaille and *Art Noveau* are predominant [2]. Estoi Palace is said to have "the finest plaster ceilings in the Algarve". Recently it has been renovated and transformed into a luxury hotel.

Garage building. Situated in the city of Leiria, district of Leiria, *center* of Portugal. It was built in the first decade of the XX century and follows the *Art Nouveau* architectonic style. Its plaster

decoration is very simple. Recently it has been transformed from a dwelling-house into a commercial area, with the façades being the only part preserved from the original structure.

Sampling. The collection of the samples can be divided in two categories: those obtained directly on site by the authors (destructive procedure), mainly referring to smooth plaster surfaces, and those obtained indirectly, as they had been detached before due to the occurrence of different anomalies in the building (only in Estoi Palace). The last ones belong mainly to the decorative plaster program. The identification and description of the samples are summarized in Table 1. Fig. 1 shows two of the studied samples.

Table 1. Description and identification of samples.

Case Study	Sample description	Identification
Estoi Palace	Decorative putty from the ceiling of the *Blue Room* (with polychromy)	A
	Decorated frame from the ceiling of the *Blue Room* (with polychromy)	B
	Decorated stucco door-face of the *Main Room* (with polychromy)	C
	Finishing plaster layer from wall of a small room, future disabled WC (with polychromy)	D
Garage Building	Finishing plaster layer from wall of 2nd floor (with polychromy)	E
	Finishing plaster layer from the same wall as sample E (with polychromy), where a wood frame was fastened	F
	Finishing plaster layer from the same wall as sample E (with polychromy)	G
	Finishing plaster layer from wall of 1st floor (with polychromy)	H
	Simple decorative frame from the top of the same wall as sample H (without polychromy)	I

Fig. 1. Photographs of samples A (left) and I (right).

Analytical methods. The mineralogical and chemical properties of the samples were determined using the analytical methodology developed by the authors Santos Silva *et al.* [3]. After a detailed visual observation of the samples and photographic register, they were dried at 40ºC for at least 12 hours and each specimen was split into several fractions to be used for different techniques.

Polished surfaces of the gypsum samples were prepared by impregnation at vacuum with an epoxy resin. They were observed with an Olympus stereo-zoom microscope and images were recorded digitally. The stereo-zoom microscope was used to study the textural properties of the existent layers in the samples (stratigraphy) and also to identify the mineralogy and morphology of the aggregates and possible pigments.

The X-ray diffraction was performed to allow a further insight on the mineralogy of the binder and other constituents such as the aggregates. A Philips X'Pert diffractometer with cobalt Kα radiation, step of 0.05º/s, between 2θ 3º and 74º was used.

The thermo-analytical techniques gave additional information on the quantitative composition of the samples, namely the relationship between the gypsum and calcite contents. A Setaram TG-DTA analyser was operated under argon atmosphere and uniform heating rate of 10º C/min from room temperature to 1000º C.

Scanning electron microscopy observations were performed on a scanning electron microscope (SEM) JEOL JSM-6400 coupled with an OXFORD energy dispersive spectrometer x-ray detector (EDX), both on polished surfaces (with backscattered electrons – BSE images) and freshly fractured surfaces (using secondary electrons – SEI images) that were sputtered with carbon in a JEOL JEE-4X vacuum evaporator or with gold-palladium film in a BALTEC sputter coater.

Some physical properties were also determined, using a methodology developed by the authors Veiga *et al.* [4,5]. The samples collected were irregular and were first cleaned of the powder and biological colonisation and maintained in a controlled environment (with 23ºC and 50% RH). The water absorption tests were performed using the technique of capillary absorption by contact [4]. In the compressive strength test, the regular shape necessary for adaptation to the compressive machine and for the calculations was achieved through the use of a confinement mortar, designed to be stronger than the analysed samples and composed by cement and siliceous sand, with volumetric proportions of 1:3 [5]. The dynamic modulus of elasticity was determined by ultrasound technique, based on the emission of high frequency sound waves and the measurement of their velocity through building materials, allowing the calculation of elastic parameters (BS 1881-Part 203).

Results and discussion

The information obtained by the visual observation of the samples is summarized in Table 2.

Table 2. Visual observation of samples.

Sample	No. of layers	Identification	Description	Presence of aggregates
A	3	A1	White preparation plaster layer, approx. 5 mm thick, applied between the mortar and the decorated piece	Perceptible
		A2.1	White plaster layer from the interior of moulded putty (A2)	Imperceptible
		A2.2	Yellow plaster from the interior of moulded putty, situated between the white - A2.1 - and the painted layer, with very irregular thickness	Imperceptible
B	3	B1	White thick plaster layer, applied over the mortar, that partially works as preparation layer for pasting of cast frames and other part has frames moulded directly during its application	Perceptible
		B2.1	White plaster layer from the interior of the frame (B2) pasted in B1	Imperceptible
		B2.2	Yellow plaster from the interior of the frame pasted in B1, situated between the white - B2.1 - and the painted layer, with very irregular thickness	Imperceptible
C	3	C1.1	Beige thick plaster layer, reinforced with sisal fibres and iron wire	Perceptible
		C1.2	Identical to C1.1, but applied over it	Perceptible
		C2	Purple-brown decorated plaster layer, with coloured “aggregates” (orange, light purple-brown)	Perceptible
D	2? 3?	D1	Beige plaster layer, applied over the mortar	Perceptible
		D2	Light yellow final plaster layer, painted in yellow and brown	Perceptible
E	1	E	Light yellow thin (1-3 mm) finishing plaster layer, painted in the same colour as the pigment of the plaster	Perceptible
F	1	F	Light pink, very thin (approx. 1 mm) finishing plaster layer	Perceptible
G	1	G	Light beige finishing plaster layer (2-3mm)	Perceptible
H	1	H	White finishing plaster layer, painted in green	Perceptible
I	2	I1	White thin plaster layer, applied between the mortar and I2	Perceptible
		I2	White plaster frame, moulded directly in the paste and painted in beige	Perceptible

The mineralogical characterization by XRD indicated that all samples are mainly composed of gypsum and calcite. Only in C2 hematite (pigment used to colour the plaster) and anhydrite can also be detected. The latter was probably used as a binder that did not rehydrate completely and not as an

aggregate, as SEM observations seem to indicate: the crystal morphology is very different between C1 and C2 (Fig. 2), while the chemical composition is similar (mainly calcium sulphate dihydrate).

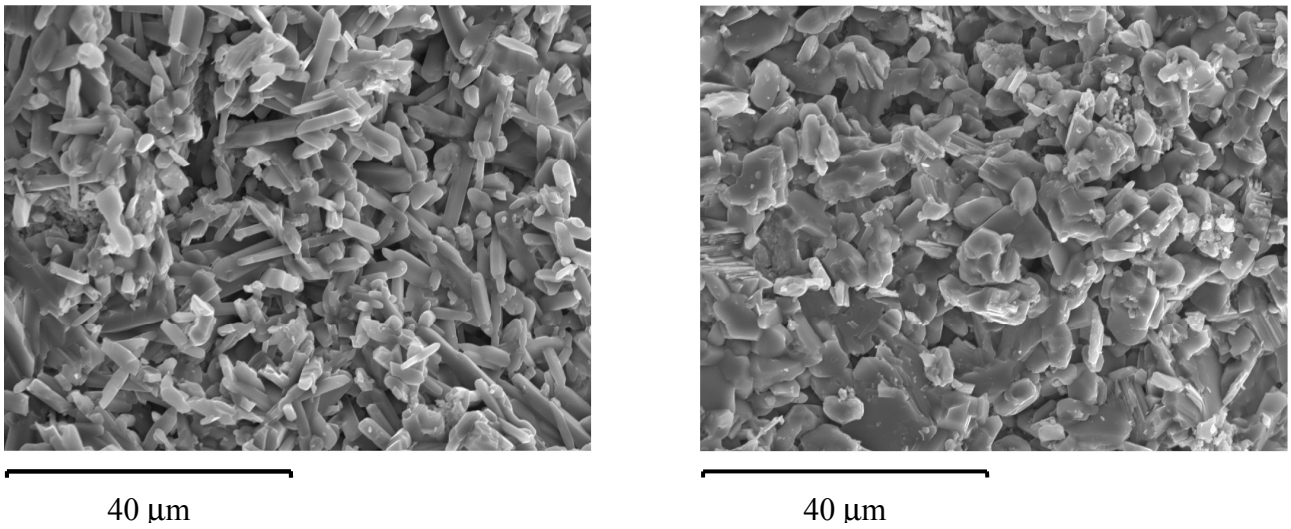

Fig. 2. SEM microphotographs of samples C1 (left) and C2 (right) (1500 X).

The aggregates, perceptible in most of the cases, are fine and of calcitic origin, as SEM observations can also confirm (Fig. 3).

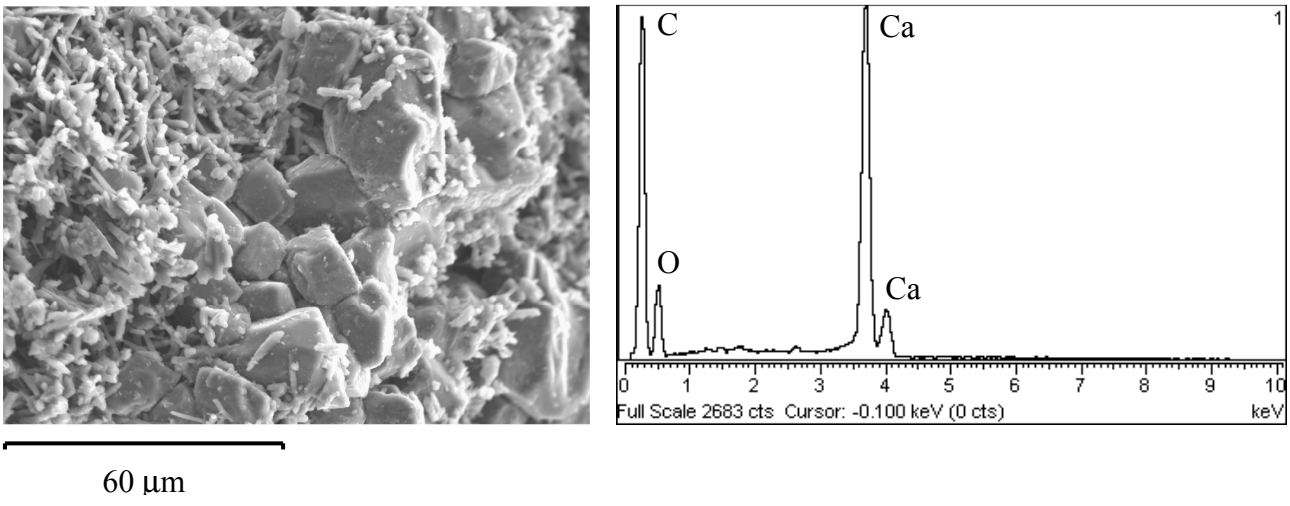

Fig. 3. Crystals of calcite used as aggregate in sample B2.2 (1000 X) and the corresponding EDS spectrum.

Thermal variations associated with the chemical and physical transformations, such as dehydration of calcium sulphate dihydrate ($CaSO_4.2H_2O$) in the range 85-250 ºC and decomposition of carbonates ($CaMg(CO_3)_2$, $CaCO_3$) in the range 600-850ºC, were obtained by TGA-DTA analysis. From these data, the amount of gypsum and calcite were calculated and the results of XRD could be confirmed (Table 3).

Table 3. Qualitative mineralogical composition of the samples (XRD) and gypsum/calcite content (TGA).

Sample	Identified crystalline compounds						Calculated gypsum and calcite contents [%]	
	Gypsum	Calcite	Quartz	Hematite	Anhydrite	Halite	$CaSO_4.2H_2O$	$CaCO_3$
A1	+++	++	-	-	-	-	63	33
A2.1	+++/++++	+/++	-	-	-	-	87	10
A2.2	+++/++++	+/++	-	-	?	-	85	15
B1	++/+++	++/+++	-	-	-	-	48	46
B2.1	+++/++++	+/++	trc	-	-	-	83	14
B2.2	+++/++++	+/++	trc	-	-	-	81	18
C1	+++/++++	+/++	-	-	-	-	87	10
C1.1	+++/++++	+/++	trc	-	-	-	87	10
C1.2	+++/++++	+/++	trc	-	?	-	87	11
C2	+++/++++	-	-	+	+	-	85	2
D1	++	+++	trc	-	-	trc	17	76
D2	++/+++	+++	+	-	-	trc	33	56
E	++	+++	-	-	-	-	19	70
F	++/+++	+++	-	-	-	-	34	62
G	++	+++	-	-	-	-	27	68
H	++	+++	-	-	-	-	31	67
I1	++/+++	++/+++	-	-	-	-	46	51
I2	++/+++	++/+++	-	-	-	-	52	46

Notation used in XRD:

++++ - very high proportion (predominant compound)
+++ - high proportion
++ - medium proportion
+ - weak proportion
trc - traces
? - unlikely presence
- - not detected

The physical properties were only determined in samples where the existing quantity allowed the execution of experimental techniques (Table 4).

In what concerns the dynamic modulus of elasticity (DME), only two samples showed values out of the moderate range (2500-4000 MPa): B1 (low) and C2 (high). Similarly, most samples showed medium compressive strengths, close to the range 1.5-2.5 N/mm^2, with the exception of B1, D and H, which showed lower values. It was not possible to test C2 separately, but the value obtained by the set C1 + C2 points to high strength for this sample, consistent with its modulus of elasticity.

The capillary coefficients were found to be much diversified: typically high for half of the tested samples and very low for the other half, probably due to the presence of organic compounds of hydrophobic behaviour, like glues and jellies [7]. The usual relationship between these characteristics - compressive strength and modulus of elasticity directly related and capillary coefficient inversely related to both of them - are not clear in these cases, due to the fact that in some cases it was not possible to test the very thin plaster layer separately from the regularization mortar, and also due to the presence of the referred organic compounds, very used for plasticity and decorative purposes. For example A2 and B2, two samples that were expected to have similar values (they are both precast gypsum plaster decorations, with very close gypsum / calcite content), show rather different compressive strength and capillarity coefficients. The irregular shape and the visible addition of additives played certainly an important role on these results. The same could be said of C2, although in this particular case the density of the sample (twice that of C1) has to be

considered and is in accordance with the respective DME and Ccc-5min results, indicating a very stiff and compact material.

Table 4. Test results of the physical properties determined and comparison with the calculated chemical content.

Sample	DME [MPa]	Compressive strength [N/mm^2]	Ccc - 5min [kg/m^{2}h$^{1/2}$]	Calculated gypsum and calcite contents [%]	
				$CaSO_4.2H_2O$	$CaCO_3$
A1	-	-	-	63	33
A2	2678	2.63	1.55	87	10
B1	1885	1.10	-	48	46
B2	3282	1.41	5.54	83	14
C1	2572	2.23	11.52	87	10
C2	9735	-	0.11	85	2
C1 + C2	-	2.66	-	-	-
D	3646	0.88	6.03	17	76
E	2846	-	0.31	19	70
F	-	1.43	6.98	34	62
G	2919	-	0.36	27	68
H	3908	1.09	3.81	31	67
I1	-	-	-	46	51
I2	2875	2.52	16.63	52	46

In the Garage building samples, the difference achieved for the compressive strengths of F and H was due to the mortar associated to the plaster finishing layer: a friable mortar in H and a better quality mortar in F, in spite of the thinner layers of mortar and stucco in this sample. The extremely low Ccc-5 min value of E and G samples can be explained by the presence of clearly non-absorbent layers: a stucco layer and a regularization mortar probably prepared with a hydrophobic agent. These and other questions will be further investigated, namely by FT-IR and GC-MS analyses of some of the samples.

Conclusions

The results obtained in this work confirmed that three groups of gypsum plasters can be considered [6]: the precast ones, technique used for the execution of more elaborated decorative pieces, were mainly composed of gypsum (> 80%) with some calcite as aggregate, which was confirmed by SEM; the pastes used for preparing a surface with a thicker layer and/or to mold directly on site simple decorations (mainly frames), had about 50% gypsum and 50% hydrated lime; finally, those plasters for application in thin layers to execute a smooth surface had approximately 20% gypsum and 80% hydrated lime.

This is valid for the two case studies considered, which means that the geographical region did not influence the composition and techniques of application of the materials.

The physical properties still need to be further investigated, but it seems, from the results already obtained, that the samples with a higher content of gypsum have better compressive strengths but higher water absorption coefficients. However, all these aspects can be affected by the use of additives, namely hydrophobic products, which were often added for functional or aesthetic reasons, a fact that probably explains the very low capillary coefficient of some samples with high contents of gypsum [7].

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