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Study of the Influence of Limewash on the Conservation of Islamic Plasterworks through Weathering Tests

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ABSTRACT
In a previous study, a layer of limewash was detected over the gypsum plasterworks used to decorate different spaces of the Real Alcázar of Seville such as interior rooms, patios and outdoor galleries. In this paper its use is analysed, namely whether it improves the properties of the plasterworks and provides a protective effect, through accelerated weathering tests designed specifically to reproduce real environmental conditions. Plaster specimens with similar composition and physical characteristics to those of the original plasterworks were prepared. After the cure of the specimens, the application of a layer of limewash was made. Samples were subjected to weathering tests that consist of water absorption cycles (by capillarity and immersion) and drying.

The results showed that the application of limewash did not improve the durability of the plaster significantly, although seemed to have a more protective effect against weathering by capillarity tests in the specimens prepared with a higher water/plaster ratio. In fact, after the immersion tests a great part of the limewash layer became detached, while in the plasterworks of the Real Alcázar this behaviour has not been observed. So, capillarity tests seem to be more adequate to reproduce the real weathering conditions of these ornamental elements.

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Durability; Gypsum; limewash; plasterwork; Real Alcázar of Seville

1. Introduction

Gypsum is a very versatile material whose main properties — ability to reproduce forms by casting or carving, fast setting, whiteness and low density — make it suitable for several applications, such as statuary or building construction, both in walls and ceilings' smooth surface coatings, as base for frescoes or in more elaborated decorative programmes. However, its drawback is its slight solubility when in contact with water (recrystallised calcium sulphate dihydrate — $CaSO_4 \cdot 2H_2O$ — solubility is 2,3 g/l at 20°C (Innorta, Rabbi, and Tomadin 1931–1936)). In addition, when humidity increases in its capillary network, it loses mechanical properties, even at low moisture contents (Coquard and Boistelle 1994; Reynaud et al. 2006; Wirsching 1985). It is consensual, however, that this effect is reversible, unless gypsum remains wet during long periods of time; in that case, it occurs the dissolution of part of the crystal structure, inducing structural changes that affect negatively the mechanical performance.

For these reasons, the extensive use of gypsum in different periods of the construction history has been mainly limited to indoor applications, sometimes mixed with other materials, like lime, aggregates or admixtures of organic and inorganic nature (Arcolao 1998; Bueno and Medina Flórez 2004; Builder 1956; Freire et al. 2010, 2016; Gárate-Rojas 1999; Genestar and Pons 2003; Hannouille 1959; Rúbio Domene 2011; Sawyer 1951; Turco and Gesso 2008). Yet, it was also used in masonry mortars, floor screeds and exterior wall coatings, usually exhibiting a higher mechanical and weathering resistance than ordinary gypsum plasters (Fischer and Vtorov 2002; Ghorab, Ragai, and Antar 1986; Igea et al. 2010, 2012; Kawiak 1991; Lucas 2003a, 2003b; Middendorf and Knöfel 1998; Philokyprou 2012; Sanz 2009).

So, it is very important to know the gypsum behaviour under different environmental conditions to understand many of the anomalies that may appear in plasterwork (Ashurst and Ashurst, 1988; Cotrim, Veiga, and de Brito 2008; Palha et al. 2012; Pereira et al. 2011; Santopuoli, Concina, and Sarmati 2012). This problem has been studied by different restorers and researchers who have been able to offer clear and relevant solutions (Ashurst and Ashurst, 1988; Freire et al. 2011; Jroundi et al. 2014; Rúbio Domene 2011; Sassoni et al. 2018).

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The main pathologies developed in the plasterworks are due to the contact with water. There are three ways in which this contact usually occurs: by *adsorption* — through the outer surface — of moisture from the air by hygroscopicity, the least aggressive form of contact; by *capillary absorption* from the interior of the building structure, i.e. water enters from the floor or from the inner face of decorative plasterwork; by *absorption of liquid water* from the outer surface during periods of rain, in the case of elements located outside, or by condensation at the surface.

The solution for the problems of solubility and loss of strength of gypsum plasters has been sought out since ancient times, proceeding till nowadays (Kondratieva et al. 2017; Pervyshin et al. 2017; Sophia, Sakthieswaran, and Ganesh Babu 2016). These properties can be improved through the addition of different materials and substances during the processes of manufacture and application or after hardening and drying by impregnating the plasterwork with waterproofing agents such as oils, varnishes, synthetic resins, acetone, arabic gum, etc. (Ashurst and Ashurst, 1988).

In the Real Alcázar of Seville the visitable spaces with plasterworks are both in internal and external areas of the monument (Figure 1), although in that case they are localized in places, called *patios*, where the direct incidence of rainwater is not frequent. However, the humidity can reach maximum values of approximately 80% on specific occasions. Considering that previous studies on the mineralogical composition of the plasterworks of the *Patio de las Doncellas* indicate that they are mainly composed of high purity gypsum (Blasco-López 2011) and that the microlayers covering their surface are, in fact, composed of one layer of limewash with 100–200 micron thickness (Blasco-López, Alejandre-Sánchez, and Flores-Alés 2015), it is important to determine the behaviour of plasterworks in this open areas and evaluate the real protective effect of the application of a layer of limewash (Figure 1B), not always consensual (Hansen et al. 2003).

So, the initial hypothesis is that the traditional application of limewash layers in plasterworks had not only an aesthetic purpose, but also a protective effect against the weathering process in plasterworks exposed to moisture (rainwater with direct incidence and humidity diffused by capillarity through the walls). To confirm that, a general methodology was adopted taking into account the environmental conditions and the type of use in the Real Alcázar of Seville. Several test specimens were prepared using commercial materials similar to the original ones. After the application of a limewash layer over the external surfaces, the two sets of specimens (with and without a limewash layer) were subjected to experimental procedures (water absorption by capillarity and water absorption by immersion) that tried to simulate the most aggressive weathering conditions they can be exposed to. Their resistance to these conditions was assessed by determining several physical and mechanical properties (porosity, water vapour permeability, compressive strength, surface hardness, ultrasonic pulse velocity) before and after the weathering tests and the results obtained are presented in this paper.

In fact, the suitability of any technique and/or treatment product and its compatibility with the original

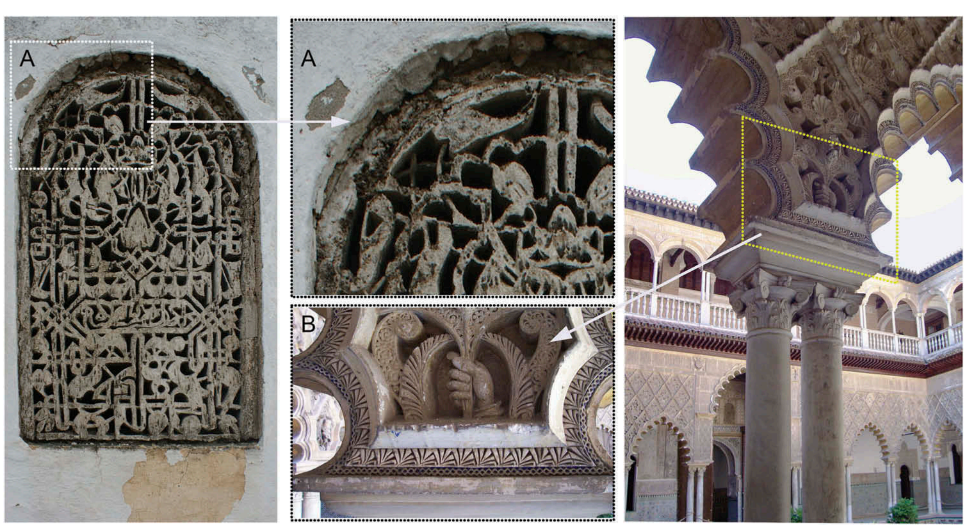

Figure 1. Decorative plasterworks elements in the Real Alcázar of Seville (Spain): A) Celosia without limewash weathered by the action of rainwater, located in the Sala de Audiencias; B) Plasterworks archery with limewash in the Patio de las Doncellas (Patio of the Maidens), in good condition.

materials or with other products used, should be evaluated (Cotrim, Veiga, and de Brito 2008; Veiga and Aguiar 2003), as well as the effectiveness of these treatments and the resistance to weathering processes and factors (Rúbio Domene 2011; Villegas 2000).

2. Materials

Previous studies of the authors show that the mineralogical composition determined by XRD of *Patio de las Doncellas* plasterworks is mostly gypsum ($CaSO_4 \cdot 2H_2O$) with traces of other mineral phases like calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), quartz (SiO_2) and celestine ($SrSO_4$). The chemical composition was also determined using FRX, as well as the main physical and mechanical properties. It was found in a cross-section study of the surface that they were covered by one layer of limewash (Blasco-López 2011; Blasco-López, Alejandre-Sánchez, and Flores-Alés 2015). The characterisation results of the plasterworks and limewash layer are summarized in Table 1.

In order to obtain test specimens with similar composition and characteristics to the original plasterworks from the Real Alcázar, a preliminary set of samples were prepared to define the final dosage. Two commercial plasters were selected: 1) B1/5/2, also known as gypsum building plaster with a setting time > 5 minutes and a compressive strength ≥ 2 N/mm^2; 2) A2, a gypsum binder for direct use on site with compressive strength ≥ 3.5 N/mm^2. Their composition and properties are established in UNE-EN 13279–1:2009 (UNE EN 13279-1 2009).

The limewash was prepared from lime putty CL90-SPL (aged for a year, with a medium particle size of 10μm, determined in Mastersizer 3000E laser particle size analyser), diluted in water until obtaining a composition of 30% $Ca(OH)_2$ and 70% H_2O in weight.

3. Methodology

The testing conditions and the sampling of the commercial products used were according to UNE EN 13279–2:2014 (UNE EN 13279-2 2014).

3.1. Samples preparation

Six types of test specimens were prepared using commercial plasters B1 and A2 with water/plaster ratios (w/p) of 0.6, 0.7 and 0.8 to determine some physical (apparent density and open porosity) and mechanical properties (Shore C surface hardness, flexural and compressive strengths). The results allowed selecting the mixes that were the most similar to the original plasterwork of the Real Alcázar.

After selection of the final materials, prismatic test specimens measuring 4x4x16 cm were manufactured and cured, as specified in the aforementioned standard, and each test specimen was cut into four pieces: two measuring 4x4x1cm and two measuring 4x4x7cm (Figure 2). These specially prepared test samples were used to determine physical and mechanical properties, and to evaluate weathering resistance by submitting them to accelerated weathering tests.

The limewash was applied on the gypsum pieces type B, and on some of the pieces types C and D of the two final mixes, being the pieces type A without limewash the references for water vapour permeability measurement, and the pieces types C and D without limewash the references for the weathering tests (Table 4). It was applied in two layers, 24 hours apart, spreading the paint in opposite directions.

Table 1. Characterisation results of the plasterworks and limewash from *Patio de las Doncellas*.

Chemical Composition (%)	Plasterwork	Mineralogical Composition: Minerals	Plasterwork	Limewash	Physical Properties	
SiO_2	0.09	Gypsum $CaSO_4 \cdot 2H_2O$	Very abundant	Trace	Real Density (g/cm^3)	2.33
Al_2O_3	0.04					
Fe_2O_3	0.07					
MnO	0.01					
MgO	0.33					
CaO	32.61					
Na_2O	0.01					
K_2O	0.02	Calcite $CaCO_3$	Trace	Very abundant	Apparent Density (g/cm^3)	1.31
SrO	0.18					
SO_3	47.14	Magnesite $MgCO_3$	Trace	–	Open Porosity (%)	43.9
LOI*	21.57					
Sum	102.07	Quartz SiO_2	Trace	–	Hardness (shore C)	81
		Celestine $SrSO_4$	Trace	–		
		Insoluble in Water residue	2.18%	–		

*LOI — Loss on ignition

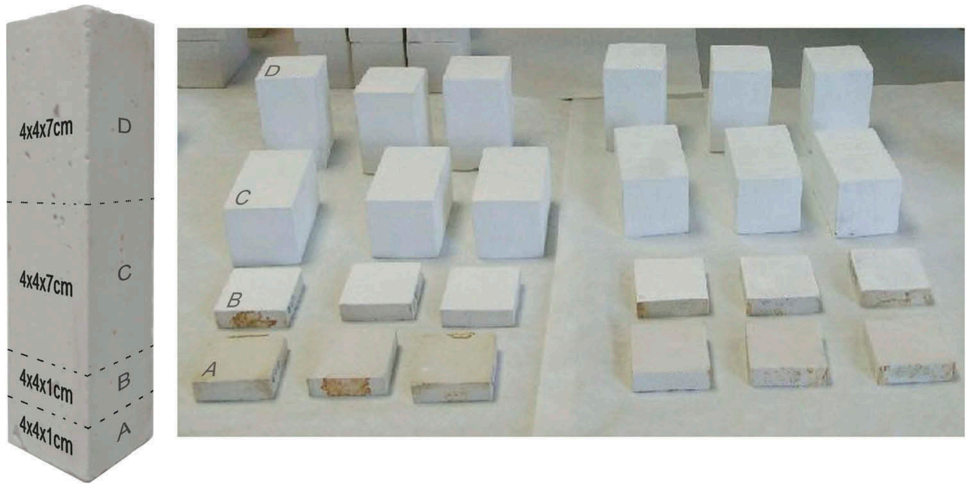

Figure 2. Types of test specimens' pieces used in the experimental work: **Type A**: pieces measuring 4x4x1cm without limewash (water vapour permeability measurement); **Type B**: pieces measuring 4x4x1 cm with limewash on the upper side (water vapour permeability measurement); **Type C**: pieces measuring 4x4x7cm with limewash on all sides except the base (4x7cm) and references without limewash (weathering test: capillary absorption); **Type D**: pieces measuring 4x4x7cm with limewash on all sides and references without limewash (weathering test: absorption by immersion).

The first layer was a thin coat of non-uniform thickness and the second one a continuous layer with a higher thickness (Lucas 1990). The layers' thickness was measured through optical microscopy after each application of limewash to ensure they were as close as possible to those found in the Real Alcázar plasterworks (between 100 and 200 microns) (Blasco-López, Alejandre-Sánchez, and Flores-Alés 2015). The progress of carbonation of the limewash layers was assessed using phenolphthalein indicator.

3.2. Weathering tests: water absorption by capillarity and immersion

Absorption of liquid water is very detrimental to gypsum based elements and it can occur by two mechanisms: *water absorption by capillarity* and *water absorption by immersion*. Both processes are followed by drying. Two weathering tests, trying to simulate these two phenomena, were designed and Types C and D gypsum pieces (with and without limewash) were subjected to the referred procedures, respectively. The alterations suffered were monitored through the observation of macroscopic and microstructural changes on the specimens as well as the determination of their physical and mechanical properties before and after the tests.

There is no standard weathering test to simulate the alteration that would be produced by the movement of water being absorbed by capillarity in one part of the pieces and evaporating at the opposite end. Therefore, a test used to measure capillary absorption in porous materials according to (UNE-EN 15801, 2010) was adapted as accelerated weathering test.

Pieces measuring 4x4x7 cm painted on five sides (type C) were placed in a container, with the unpainted side over a 1 cm layer of blotting paper soaked in water. The same procedure was applied to unpainted pieces (Figure 3a). The rise of water by capillarity occurs from the contact side towards the free sides where it evaporates; creating a continuous flow of water that can solubilize small amounts of calcium sulphate and transport them to the surface, where they will precipitate. Water was periodically added to maintain a constant level. The test lasted 40 days at ambient temperature (20 ± 2ºC). The specimens were weighed every two days being water saturated.

The purpose of the accelerated weathering test due to water absorption by immersion was to simulate the effect of contact with large amounts of water, alternating with drying periods. The thermo hygrometric test employed to study treatments for stone materials was adapted (Villegas 2000), using a lower drying temperature to avoid changing the equilibrium phase of calcium sulphate. The test comprised 13 cycles consisting of 6 hours of immersion in water at 20 ± 2°C, oven drying at 40 ± 2°C for 41 hours, 1 hour for cooling and weighing. Ultrasonic pulse velocity was measured at the end of the procedure (Figure 3b). Three pieces Type D painted on every side and three unpainted pieces used as reference were submitted to this test.

3.3. SEM observations

In order to have further insight into the microstructural changes of the tested pieces, SEM observations of samples from the original plasterworks of *Patio de las*

(a) (b)

Figure 3. Weathering tests: a) Capillary water absorption, b) Absorption by immersion.

Doncellas, as well as of the unweathered and weathered pieces of plaster B1, with water/plaster ratios (w/p) of 0.6 and 0.8, were made. A Jeol JSM 6460-LV microscope equipped with an energy-dispersive X-ray (EDX) microprobe and beryllium ATW2 window was used. SEM images in both secondary electron mode (SE) and in back-scattered electron mode (BSE) were acquired from gold-coated pieces.

3.4. Physical properties

Open **porosity** and **apparent density** were obtained by vacuum water saturation of the material, according to the standard (UNE EN 1936, 2007). The results were calculated taking the average of three pieces.

The **water vapour permeability test** is a standard procedure with different variants depending on the water vapour that enters or leaves the container, which maintains drier or more humid hygrometric conditions than the environment. In this case, the "wet glass" method was used which is based on the measurement of the water vapour flux through the sample due to the pressure differential between the internal (relative humidity approximately 100%) and the external surface conditions (a temperature of 20 ± 2°C and a relative humidity of 50 ± 5%). It involved the use of a container filled with water until its level reached 20 mm below the inner surface of the test piece applied on the top. The contained was perfectly sealed so that water vapour could only go out by passing through the gypsum piece (Figure 4a). The permeability coefficient is defined as the amount of water vapour flowing through the specimen per time unit and per unit area, and can be calculated from the

(a) (b)

Figure 4. a) Containers with specimens for water vapour permeability test, b) Ultrasonic pulse velocity measurement.

weight loss of the container over time. The values corresponding to each piece were corrected according to the respective thicknesses, in order to keep a constant reference of 1 centimetre and they were also corrected for ambient temperature (18-22ºC) so that they were always expressed at 20ºC, using Equation (1):

$$K_g = (20^\circ C,\ 1cm) = K_g(\exp) \cdot \frac{P^0_{H2O}(T_{\exp})}{P^0_{H2O}(20^\circ C)} \cdot \frac{sample\ thickness(cm)}{1\ cm} \quad (1)$$

Pieces of 4x4x1cm limewashed (type B) on one side were used for this test and they were compared with unpainted pieces used as control (type A).

The water vapour permeability was also measured in previously weathered specimens: 4x4x1cm plates were cut from the 4x4x7cm pieces that had been subjected to the aforementioned tests. Two pieces were used for each type and dosage. An average permeability coefficient was obtained. The procedure was carried out during one week and the weight data for each container were collected approximately every 24 hours.

The **ultrasonic pulse velocity test** consisted on the measurement of the velocity of high frequency sound waves passing through the material. Vibration was generated and received by an electromechanical recorder. This technique measured the interval of time between the introduction of vibration and its reception. Knowing this data and the distance between the probes, the transmission rate of the sound waves was calculated. Velocity is related to the elastic modulus and increases with the latter, so one of the applications of this measurement is to indicate gypsum physical or mechanical deterioration. Six measurements have been made in each case. These measurements were taken by an Ultrasonic-Tester BP5 device, measuring the test pieces of 4x4x7cm in longitudinal position, placing the two probes at each end of the piece and using modelling clay as a coupling (Figure 4b). The samples were dried at 40 ± 2ºC, until constant weight, before the measurements.

3.5. Mechanical characterisation

After drying the pieces at 40 ± 2ºC, **surface hardness** was determined using a Härtoprüfer Shore C durometer, according to the standard UNE 102–039-85 (UNE 102-039 1985). The procedure consisted of measuring the resistance of the material to the penetration of a conical needle attached to a shaft with a gear, which applied a given strength to the surface. Shore C hardness is directly related to the depth of penetration of the needle and is measured in a scale of 0–100 units. Ten measurements have been made in the limewashed sides after capillarity and immersion tests and compared with the initial value without limewash. The initial hardness of the painted pieces was not measured in order to avoid any potential deterioration of the lime layer that could occur by compressing the surface with the durometer.

The **flexural and compressive strengths** were measured with a testing machine TCCSL model PCI-30t, using a load cell of 300 kN and a loading speed of 1N/mm^2, following the procedure outlined in UNE- EN 13279–2:2014 (UNE EN 13279-2 2014).

4. Results and discussion

4.1. Commercial plasters characteristics

Both hydrated plasters' chemical composition, determined by XRF, is shown in Table 2. The results reveal a composition enriched in SO_3 and CaO, attributable in these cases to the dihydrate ($CaSO_4 \cdot 2H_2O$) content, and a loss on ignition of approximately 21%. Plaster A2 had higher purity than plaster B1.

The mineralogical composition determined by XRD was very similar for both unhydrated plasters, containing mainly bassanite ($CaSO_4 \cdot ½H_2O$), and anhydrite ($CaSO_4$) in a lower percentage. They were also identified traces of calcite and dolomite but are assigned to impurities from the raw materials. For hydrated plasters, the transformation of bassanite and anhydrite into gypsum can be observed (Figure 5).

4.2. Selection of samples

As commented previously, six types of samples were prepared to select the most similar to the materials found in the Real Alcázar. The physical and mechanical characteristics of plasters B1 and A2 with w/p ratios of 0.6, 0.7 and 0.8 are shown in Table 3.

The specimens and dosages tested suggest that B1-0.6 is the closest to the properties of the plasterwork of *Patio de las Doncellas* (Table 1), so it was selected for this study. However, considering the previous knowledge of other plasterworks' properties exposed to an external environment in the Real Alcázar, such as the *Patio del Yeso* and the *Cenador de la Alcoba* (Blasco-López 2011; Blasco-López, Alejandre-Sánchez, and Flores-Alés 2015), it was also decided to select test specimens B1-0.8, with more close characteristics to these ones.

Table 2. Chemical composition (%) of the commercial plasters types B1 and A2 after hydration.

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	SrO	P_2O_5	SO_3	LOI	TOTAL
B1	2.63	0.79	0.24	0.01	1.09	33.26	0.08	0.19	0.08	0.16	38.61	21.92	99.06
A2	1.42	0.38	0.16	0.01	0.98	32.51	0.08	0.14	0.13	0.02	42.88	20.41	99.12

The sets of samples of the two final mixes used for the weathering tests were prepared as indicated in Figure 2 and in Table 4.

4.3. SEM microstructural analysis

Images of the microstructures of one sample of the plasterwork of *Patio de las Doncellas* and of the mixes B1-0.6 and B1-0.8 are shown in Figure 6. Gypsum crystallises in prismatic structures of the monoclinic system with different habits. In the sample of the original plasterwork, tabular crystals of very small size (less than 5 micron) form a tight and homogeneous microstructure (Figure 6a), while in B1-0.6 and B1-0.8 it is possible to observe the existence of crystals of tabular and acicular habit with different elongations (length/width ratio): thicker and shorter (about 10 micron) in the case of B1-0.6 (Figure 6b), forming a quite homogeneous microstructure; thinner and longer (sometimes with several tens of micron) in B1-0.8 (Figure 6c), forming a more porous and less organised matrix.

These observations confirm that gypsum plasters produced with lower water/plaster ratios have a smaller void fraction and higher bonding between crystals, showing better mechanical performance (Coquard et al. 1994; Yu and Brouwers 2011) (Table 3). They also allowed concluding that B1-0.6 has a microstructure more similar to that of the plasterwork of *Patio de las Doncellas* than B1-0.8, in accordance with the results obtained for the physical and mechanical properties of both (Tables 1 and 3)

4.4. Weathering tests: water absorption by capillarity and immersion

The results of the weathering tests were evaluated by comparing different characteristics of the specimens before and after being subjected to the experimental procedures: weight, open porosity, water vapour permeability, surface hardness, ultrasonic pulse velocity and compressive strength. The visual inspection was also made.

During the capillarity test, it was observed that the test specimens were becoming saturated without changes occurring on the sides that were not in contact with the water layer. The final weight was obtained after drying the specimens at 40 ± 2°C. Table 5 shows that the weights underwent very small variations during the test due to the low level of deterioration of the specimens.

The unpainted pieces with w/p = .8 did not suffer losses of material by dissolution, while the pieces with

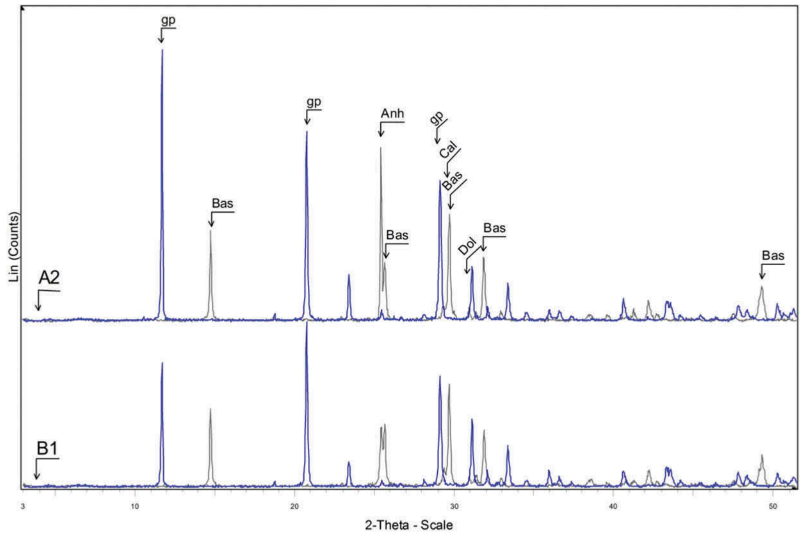

Figure 5. Diffractograms of the commercial plasters types B1 and A2 used (grey unhydrated and blue hydrated). Gp = gypsum; Bas = bassanite; Anh = anhydrite; Cal = calcite and Dol = dolomite.

Table 3. B1 and A2 plasters properties with 0.6, 0.7 and 0.8 w/p ratios.

Plaster -w/p	Apparent density (g/cm^3)	Open Porosity (%)	Hardness (shore C)	Flexural strength (MPa)	Compressive strength (MPa)
B1-0.6	1.31	45.47	83	3.75	10.15
B1-0.7	1.14	52.92	73	1.86	5.61
B1-0.8	1.07	54.87	62	1.50	4.10
A2-0.6	1.23	47.79	88	5.13	14.04
A2-0.7	1.07	53.99	76	3.32	7.96
A2-0.8	0.99	57.93	69	2.53	6.31

w/p = .6 did. In the painted pieces, deterioration occurred in the parts of the vertical faces that were in contact with the water soaked paper: the detachment of little fragments of the limewash coat on the first 3 mm was observed. These losses of paint explain the differences of weight before and after the test (Table 5).

In the immersion test, the untreated pieces showed higher dissolution of gypsum, whose presence was visible in the water where they were immersed. This was reflected in the weight loss of the pieces at the end of the test (Table 5) and by increased surface roughness. On the painted specimens, limewash layers were also deteriorated due to water immersion, with the detachment of great fragments of the coat on all sides (Figure 9). However, the weight loss was smaller (Table 5). SEM observations allowed clarifying both features: (i) a void fraction due to gypsum dissolution appeared in the interface between gypsum and limewash (Figure 7), weakening the

Table 4. List of standard test specimens and pieces made for plaster B1 and w/p ratio of 0.6 (the same for samples B1 with w/p 0.8).

3 specimens per mould	4x4x 16 cm test specimens	4x4x7 cm Pieces types C- D	4x4x1 cm Pieces types A-B	Paint
Mould1-B1 $_{0.6}$	Specimen B1$_{0.6}$ (1)	B1$_{0.6}$ Immersion (1)	B1$_{0.6}$ Permeab. (1)	Limewash
		B1$_{0.6}$ capillarity (1)		Limewash
	Specimen B1$_{0.6}$ (2)	B1$_{0.6}$ Immersion (2)	B1$_{0.6}$ Permeab. (2)	Limewash
		B1$_{0.6}$ capillarity (2)		Limewash
	Specimen B1$_{0.6}$ (3)	B1$_{0.6}$ Immersion (3)	B1$_{0.6}$ Permeab. (3)	None
		B1$_{0.6}$ capillarity (3)		None
Mould2-B1 $_{0.6}$	Specimen B1$_{0.6}$ (4)	B1$_{0.6}$ Immersion (4)	B1$_{0.6}$ Permeab. (4)	Limewash
		B1$_{0.6}$ capillarity (4)		Limewash
	Specimen B1$_{0.6}$ (5)	B1$_{0.6}$ Immersion (5)	B1$_{0.6}$ Permeab. (5)	Limewash
		B1$_{0.6}$ capillarity (5)		Limewash
	Specimen B1$_{0.6}$ (6)	B1$_{0.6}$ Immersion (6)	B1$_{0.6}$ Permeab. (6)	None
		B1$_{0.6}$ capillarity (6)		None
Mould3-B1 $_{0.6}$	Specimen B1$_{0.6}$ (7)	B1$_{0.6}$ Immersion (7)		Limewash
		B1$_{0.6}$ capillarity (7)		Limewash
	Specimen B1$_{0.6}$ (8)	B1$_{0.6}$ Immersion (8)		Limewash
		B1$_{0.6}$ capillarity (8)		Limewash
	Specimen B1$_{0.6}$ (9)	B1$_{0.6}$ Immersion (9)		None
		B1$_{0.6}$ capillarity (9)		None
Mould4-B1 $_{0.6}$	Specimen B1$_{0.6}$ (10)	Reserved (10)		
	Specimen B1$_{0.6}$ (11)	Reserved (11)		
	Specimen B1$_{0.6}$ (12)	Reserved (12)		

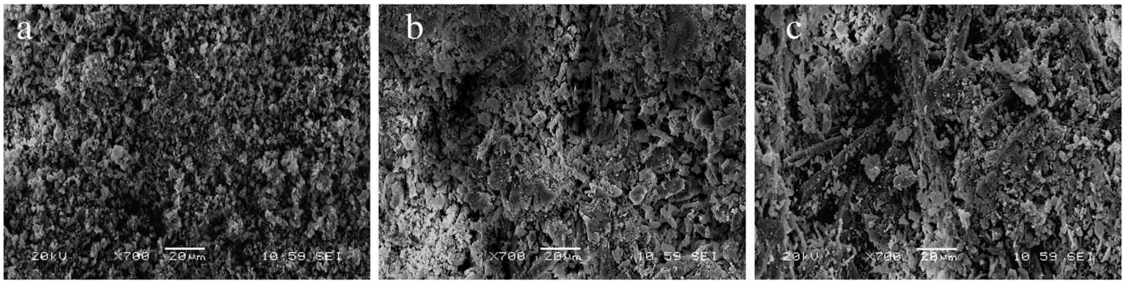

Figure 6. SEM images of the plasterwork of *Patio de las Doncellas* (a), B1-0.6 (b) and B1-0.8 (c).

Table 5. Average weight (g) of 3 pieces before and after the capillarity and immersion tests.

	Capillarity test (g)					
	Untreated			Type C (limewash)		
w/p ratio	Initial	Final	Δ (%)	Initial	Final	Δ (%)
0.6	127.1	125.0	− 1.65	129.8	128.5	− 1.00
0.8	109.2	109.2	0.00	114.1	112.7	− 1.24
	Immersion test (g)					
	Untreated			Type D (limewash)		
	Initial	Final	Δ (%)	Initial	Final	Δ (%)
0.6	126.6	118.9	− 6.08	125.7	125.4	− 0.23
0.8	108.7	103.1	− 5.15	112.6	111.7	− 0.84

connection between layers and leading to detachment in some areas; (ii) the limewash layer is less soluble than gypsum and its porous structure is much more compact, so it probably acted as a barrier against the diffusion of the solubilized gypsum. This hypothesis is supported by the presence of many gypsum prismatic crystals in the limewash matrix (Figure 7b).

Table 6 shows the **open porosity** values obtained before and after the weathering tests. On samples 0.6 the changes in porosity were below 1%, which can be considered not significant. Nevertheless, pieces 0.8 suffered an important decrease in porosity that may be related to the dissolution of gypsum and recrystallization with different crystal size, supported by the SEM observations (Figure 8a and b for capillarity test and Figure 8c and d for immersion test), thus affecting the total volume of pores after the tests. In fact, a higher initial porosity allows a greater contact surface between water and gypsum, so that the quantity of dissolved gypsum is higher and so is the recrystallisation during drying, causing more alterations on the porous structure. Again, the presence of limewash has limited the loss of gypsum by dissolution, increasing the effect of recrystallisation and contributing to a slightly more accentuated decrease of porosity.

The **water vapour permeability** has been expressed as an average permeability coefficient determined on pieces unpainted (type A) and limewashed (type B), and on pieces of 4x4x1cm resulting from the accelerated weathering tests. The results obtained are shown in Table 6. The water vapour permeability coefficients for all the weathered pieces increased when compared to the pieces not weathered, especially after the capillarity

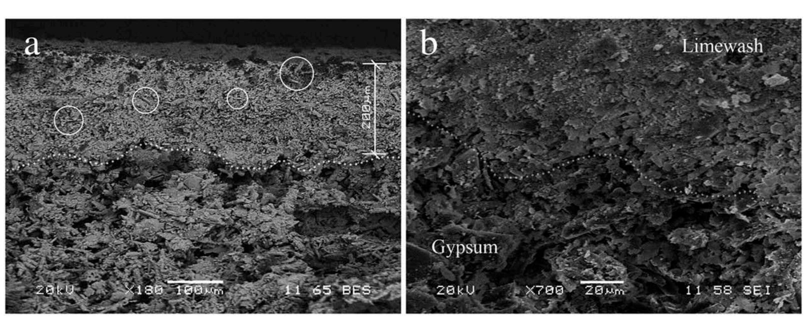

Figure 7. Limewash section on piece type D after immersion test: a) Void fraction in the interfacial zone and crystallization of thin prismatic crystals of gypsum on the limewash layer (white circles); b) Detail of interfacial zone (dotted line) between limewash and gypsum.

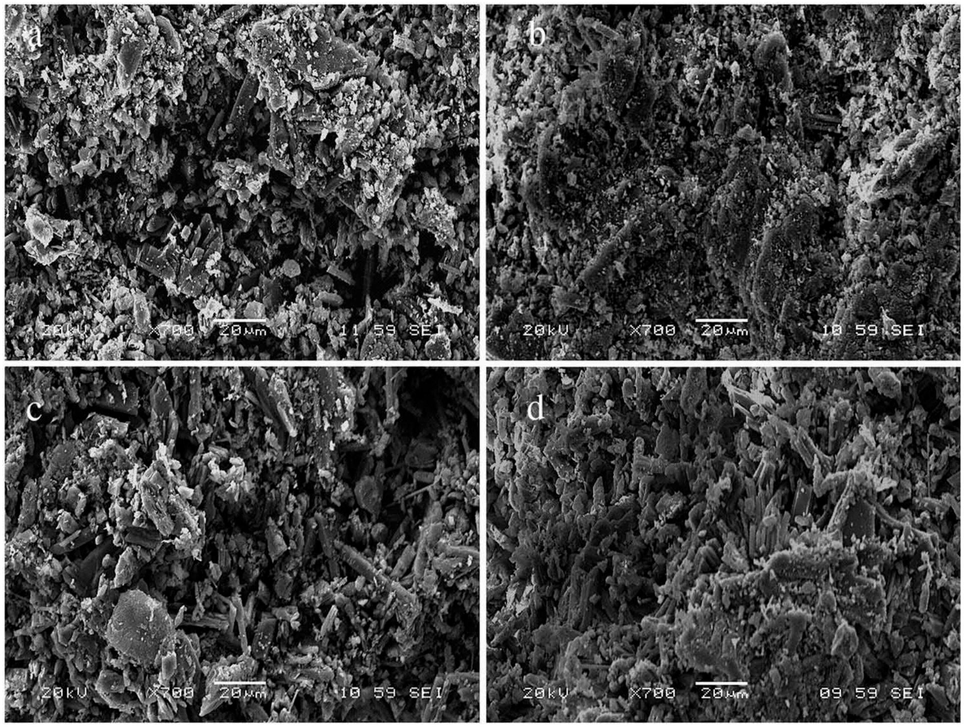

Figure 8. SEM-SE images of B1-0.8 limewashed type C and D pieces: a) Internal zone, after capillarity test; b) Internal zone, near the limewash layer, after capillarity test; c) Internal zone, after immersion test; d) Internal zone near the limewash layer, after immersion test.

Table 6. Physical and mechanical properties before and after the weathering tests.

Average open porosity (%)						
w/p ratio	Treatment	Initial	After capillarity test (type C)	Δ (%)	After immersion test (type D)	Δ (%)
0.6	Untreated	48.11	48.09	-0.04	47.66	-0.93
	Limewash		48.27	0.33	48.48	0.76
0.8	Untreated	59.90	56.60	-5.51	56.12	-6.31
	Limewash		54.70	-8.68	54.75	-8.60
Water vapour coefficient (g/m^2·d)						
0.6	Untreated	103	230	123.30	189	83.90
	Limewash	106	214	101.88	186	75.49
0.8	Untreated	118	279	136.44	205	73.73
	Limewash	97	202	108.25	191	96.91
Ultrasonic pulse velocity (m/s)						
0.6	Untreated	2246	2188	-2.58	2226	-0.89
	Limewash	1960	2061	5.15	2099	7.09
0.8	Untreated	1972	1962	-0.50	1940	-1.62
	Limewash	1784	1920	7.62	1838	3.03
Surface hardness (Shore C)						
0.6	Untreated	76.0	79.7	4.86	73.6	-3.15
	Limewash		81.0	6.57	78.9	3.81
0.8	Untreated	60.0	64.9	8.16	60.8	1.33
	Limewash		71.5	19.16	64.0	6.66
Compressive strength (N/mm^2)						
0.6	Untreated	8.61	7.89	-8.36	6.39	-25.78
	Limewash		7.01	-18.58	4.93	-42.74
0.8	Untreated	4.74	4.43	-6.54	3.19	-32.70
	Limewash		4.86	2.54	3.99	-15.82

test. A plausible explanation, supported by the images in Figure 8a and b is that the water, while continuously rising along the pieces, dissolves part of the gypsum and creates preferential paths that are more porous or contain larger pores, thus facilitating vapour flow.

The water movement is different in the immersion test, so this increment is less accentuated. In general, the water vapour permeability increase was slightly smaller in the painted pieces, probably because the lower porosity and pore sizes observed in SEM images

Figure 9. Specimens Type D after immersion test.

of the limewash layer limited the rate of evaporation of water (Figures 7a and b).

The **ultrasonic pulse velocity (UPV)** of the specimens before and after being subjected to the two weathering tests is shown in Table 6. It can be seen that the UPV of the untreated pieces only decreased slightly for both w/p ratios, but it increased in the limewashed specimens. Considering the configuration of the UPV test, the size and shape of the pieces and the surface area of the probes, the most probable hypothesis is that the transmission of the ultrasounds has been made by the limewash coating and the superficially recrystallised gypsum (Figure 8b), instead of being carried out through the piece.

The **surface hardness** results are shown in Table 6. After the weathering tests, this parameter was measured on the remaining lime layers that were still well bonded to the specimens. In general, it was observed that hardness increased in all types of pieces, with larger increases in those subjected to the capillarity test. This can be due to the recrystallisation of gypsum close to the surface of the pieces after it was dissolved by the passage of water (Figure 8a and b). For treated specimens, this effect is reinforced by the calcium carbonate coating. In the 0.8 w/p ratio specimens the effect of this phenomenon in the surface hardness results is more accentuated since they have initial lower values and a very probable higher recrystallization effect.

Finally, Table 6 also shows the **compressive strength** values (average of two pieces type D), before and after the weathering tests. In general, it can be seen that greater initial compressive strength (0.6 w/p ratio) led to higher decrease for both tests. It was also observed that after the immersion test the loss of strength is more significant, probably due to the higher gypsum dissolution that this test involves (Table 5). As observed with the results of other parameters, the limewash seems to have a more positive contribution in the specimens with higher w/p ratio, where the compressive strength even increased after the capillarity test.

Concerning a previous study where the application of protection products to gypsum plasters was made (using two different concentrations and applied in 3 and 7 layers) and the respective resistance to weathering tests (also focused on the action of cycles of absorption of water and drying) was evaluated (Rúbio Domene 2011), it can be said that it did not show better results.

With the exception of one product (Arabic gum), all the others were based on synthetic resins, needing the use of organic solvents to be prepared. Nevertheless, the great majority of the specimens showed losses of mass due to dissolution of gypsum of the same order of magnitude as those observed in the present study, more pronounced in the cases of lower product concentration and application in 3 layers, where the protection disappeared from the surface of the plaster during the weathering tests. No other physical or mechanical properties were tested. The unquestionable environmental and human drawback that the use of synthetic products represent and the few benefits observed when compared to the application of a limewash layer, lead to the conclusion that this method is not more advantageous. Other studies on the increase of gypsum plasters resistance towards the action of water comprehend the use of consolidation products that react with gypsum, forming less soluble materials (Sassoni et al. 2018). Although it was observed a decrease in mass loss, it was smaller than expected, due to the low depth of penetration, still a problem to solve. The most promising methods seem to be those based on bio cementation, using bacterial bio mineralization of calcium carbonate (Jroundi et al. 2014): the bio material formed is not depth dependent and it does not affect significantly the porosity and the pore size distribution of the original matrix, while increasing the mechanical resistance. However, further studies are needed concerning the behaviour towards weathering.

5. Conclusions

As expected, the main conclusion of this study is that the weathering tests proved to be useful, inducing significant changes in the properties of the gypsum plaster. The immersion test mainly affected the compressive strength and the capillarity test had a greater influence in the surface hardness and water vapour permeability.

The substantial changes that occurred in the physical and mechanical properties of the materials are not always associated with the variation of porosity after the weathering. In general, w/p = .6 specimens showed small changes in porosity but had an important decrease in compressive strength and an increase in surface hardness and water vapour permeability, while in w/p = .8 specimens a significant decrease in porosity was observed, possibly associated with a more accentuated gypsum recrystallisation process and in accordance with a better behaviour concerning the compressive strength, surface hardness and water vapour permeability.

It was shown that the application of a limewash layer in the unweathered pieces did not contribute significantly to hinder the moisture from escaping in the form of vapour; after the weathering tests this capacity has increased quite significantly.

The limewash showed a more protective effect against weathering in the specimens prepared with a higher w/p ratio, especially in the weathering by capillarity tests. This test seems to be more adequate to reproduce the real weathering conditions of these ornamental elements. In fact, after the immersion test a great part of the limewash layer became detached, while in the limewashed plasterworks of the Real Alcázar this behaviour has not been observed, because the weathering conditions are not as extreme as those of the proposed tests.

The application of a limewash layer is advantageous when compared to the use of other methods, namely the application of synthetic based products, not significantly more durable and effective and definitely more toxic and aggressive to the humans and to the environment.

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