Journal of Cultural Heritage 14 (2013) 169–173

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Case study

Porosity and surface hardness as indicators of the state of conservation of Mudéjar plasterwork in the Real Alcázar in Seville

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ARTICLE INFO

Article history:
Received 2 January 2012
Accepted 13 April 2012
Available online 16 May 2012

Keywords:
Real Alcázar
Plasterwork
Shore C hardness
Porosity
Conservation

ABSTRACT

Plasterwork, a very typical element of Islamic art, comprises highly artistic decorative elements on wall, arches, and vaults. Due to their gypsum composition, such elements are easily weathered, primarily because of low mechanical strength and slight solubility in water. This work has studied the traditional Islamic plasterwork in the halls and patios of the Mudéjar Palace (13–16th centuries) in the Real Alcázar of Seville. This palace complex was declared a World Heritage Site by UNESCO in 1987. The analysis of its porosity and shore C surface hardness has allowed determination of the mathematical correlation between them. Consequently, future evaluations can merely measure the hardness (a non-destructive test) to estimate the plasterwork's porosity (which reveals its mechanical strength and its degree of weathering). These elements must be maintained in order to prevent the spread of pathologies. In addition to requiring an in-depth knowledge of its materials, application techniques, and properties, to do so also demands simple techniques for regular assessments and criteria to prioritize interventions if they become necessary.

1. Artistic background and research aims

Plasterwork consists of decorative elements typical of Islamic art, applied on walls, arches, and vaults. It tends to extend over large surfaces to cover adobe or brickwork and comprise unlimited series of repetitive motifs. Gypsum, an essential component of plasterwork, is abundant in nature and easy to work. Consequently, it is one of the earliest materials used by man in building construction. Gypsum, however, is a fragile material with poor mechanical and structural strength since it is relatively soft and easily weathered by the elements. Therefore, the plaster facings would have required continual maintenance from the moment they were put up [1].

The aim of this work was to study the main Islamic plasterwork in the Real Alcázar of Seville palace, focusing on knowledge of porosity and surface hardness of the plasterwork to develop non-destructive testing (NDT) procedures to aid in future determinations of their degree of weathering in the monument's halls and patios. Efforts have been made to determine means of preservation that can also be extrapolated to other monuments with similar ornamental motifs.

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http://dx.doi.org/10.1016/j.culher.2012.04.010

2. Gypsum porosity origin: the water demand of β-hemihydrate

Equation (1) shows the chemical hydration of hemihydrate. According to its stoichiometry, the amount of water necessary to hydrate 100 g of hemihydrate and transform it into gypsum is 18.6 g:

$$CaSO_4 \cdot 0.5H_2O + 1,5H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad (1)$$

But the water that the plaster needs for rehydration is much lower than that necessary for the batching. Therefore, the excess evaporates during the setting and hardening, leaving a porous microstructure in the rehydrate. As an example, a semi-hydrated batch with a water/hemihydrate ratio of 0.6 has 60 g of water for every 100 g of semi-hydrated plaster, although only 18.6 g of water are actually used in the hydration reaction. As a result, the plasters used for these works tend to have high open porosity (41–65%), and are consequently classed as very porous materials [2].

Yu and Brouwers [3] studied the microstructure of the β-hemihydrate hydrating system and proposed a void fraction model that is related to the water content and the degree of hydration of the hydrating system, finding good agreement between predicted values and experimental data. The authors described a non-linear

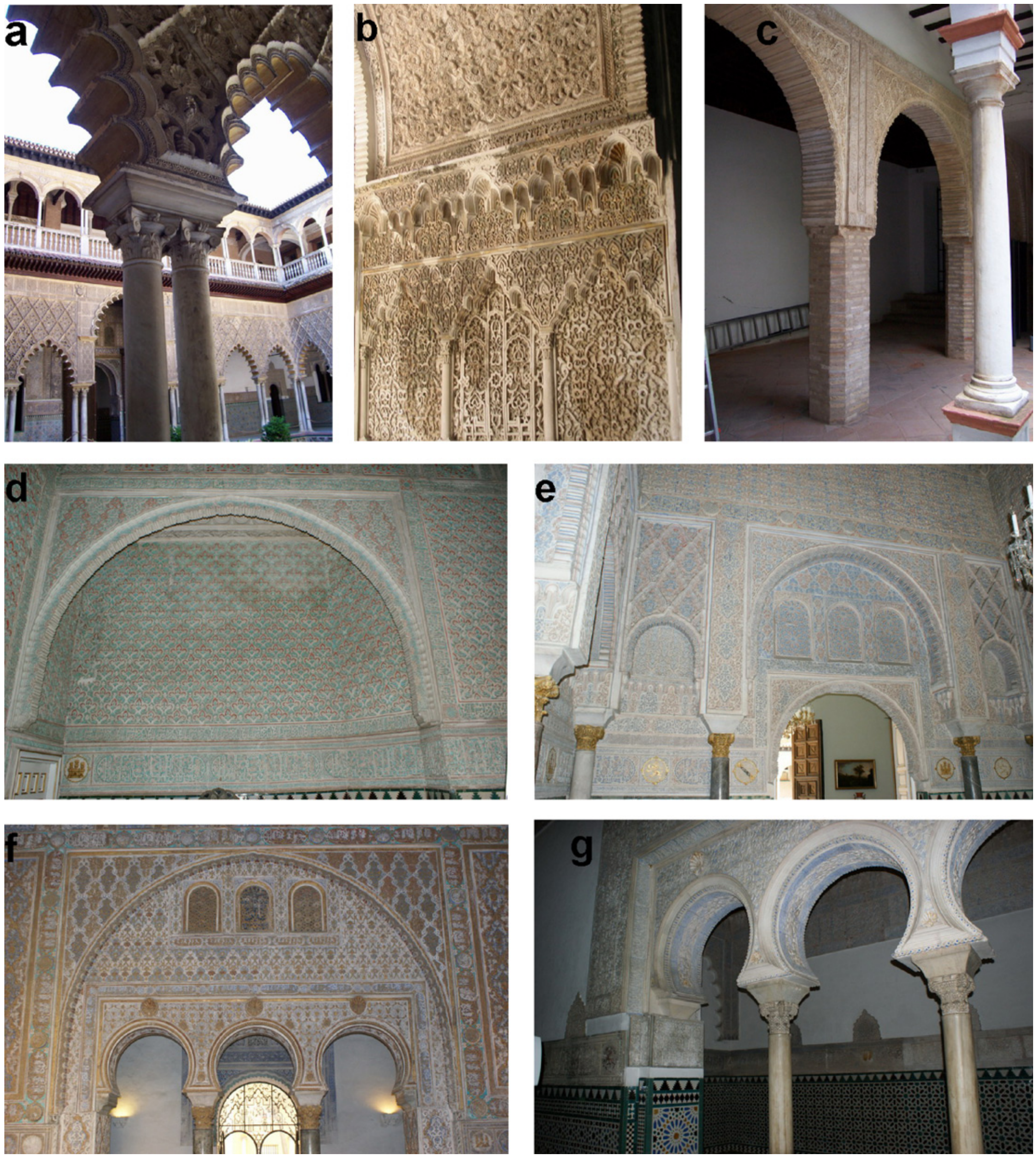

Fig. 1. Representative Mudéjar plasterwork: a: ogival arches on Corinthian-style columns in the Patio of the Maidens (GPD); b; detail of the eastern opening of the Justice Hall with ataurique topics (mocárabe frieze) with smooth kufic and palmette logotypes, with flowers and fingerlike impressions from the Almohad tradition (GSJ); c: Mudéjar arches in the Patio of the Sun (GPS), next to the 18th century arcade (on the right); d: scalloped arch and ataurique plasterwork on one of the walls of King Pedro's bedchamber (GDR); e: three-part sketch of the Audience Hall, with sebka and ataurique on its walls (GSA); f: spandrels in the decorative scalloped arch framing keyhole arches with three tracery windows above them in the Ambassadors Hall (GSE); g: inner façade hall-side room of Royal Bedchamber (GCR).

Table 1
Reference for samples, location, and possible construction period.

Number	Case study-location	Sample designation	Ornamental and decorative art	Possible construction period and style
1	Patio of the maidens (lower inner gallery ajimez)	**GPD**	Ajimez plasterwork	14th–16th centuries Mudéjar
2	Patio of the sun (restored zone)	**GPS**	Frieze plasterwork	20th century restoration
3	Justice Hall (northeastern headwall arch)	**GSJ**	Arch plasterwork	14th century Mudéjar
4	Royal bedchamber (inner façade hall-side room)	**GCR**	Panel plasterwork	14th–20th centuries Mudéjar
5	Alcoba Pergola (southern core)	**GCA**	Arch plasterwork	14th-16th centuries Mudéjar
6	Prince's room (northeastern arch)	**GCP**	Arch plasterwork	14th–16th centuries Mudéjar
7	Patio of the dolls (northeastern headwall)	**GPM**	Sebka plasterwork	14th–19th centuries Mudéjar
8	Ambassadors hall (arch separating roof of Philip II)	**GSE**	Arch plasterwork	14th century Mudéjar
9	Patio of the sun	**GPS2**	Spandrel plasterwork	13th–14th centuries (?) Mudéjar
10	Justice Hall (access from Montería)	**GSJ2**	Arch plasterwork	14th century Mudéjar
11	Patio of the sun (zone other than the above)	**GPS3**	Arch plasterwork	13th–14th centuries (?) Mudéjar
12	Catholic monarchs hall (arch east of P. Dolls)	**GSR**	Arch plasterwork	16th–19th centuries Mudéjar
13	Hall of Philip II roof (Pavones Arch)	**GSF**	Spandrel and arch plasterwork	16th century Mudéjar
14	Hall of Charles V roof (arch separating room)	**GSC**	Arch plasterwork	14th–16th centuries Mudéjar
15	King Pedro's bedchamber (eastern headwall arch)	**GDR**	Arch plasterwork	14th–16th centuries Mudéjar
16	Audience hall or chamber (north central arch)	**GSA**	Arch plasterwork	14th century Mudéjar

equation to relate the void fraction with the water/hemihydrate ratio as follows:

$$\varphi = \frac{\frac{w}{h} - 0.13}{0.38 + \frac{w}{h}} \quad (2)$$

where φ is the void fraction and w/h is the water/hemihydrate ratio.

As expected, the void fraction is directly related to the water/hemihydrate ratio (w/h), so that the higher the water to hemihydrate ratio, the greater the void fraction.

3. Mechanical properties of gypsum and porosity

3.1. Mechanical strength

Schiller [4] was the first author to propose a model to describe the relation between the void fraction and the strength of gypsum, reporting a critical void fraction of 0.79, at which value the gypsum loses its strength. The void fraction of the gypsum increases when the w/h ratio increases, which in turn leads to a weaker bond between the gypsum crystals [3]. From the above it is plain that, the greater the porosity of a plaster, the greater the amount of water that was used in its manufacture (which may be related to the technique used), and the lower the compactness, apparent density, and mechanical strength of the set product.

Yu and Brouwers [3], applying β-hemidrate, compared several models proposed to describe the relation between the void fraction and the flexural and compressive strength of gypsum, obtaining a critical void fraction value of 0.73–0.77. These values are in line with Schiller [4] and indicate that the strength is independent of the type of hemihydrate used (models used α-hemihydrate).

No bibliographic references have been found indicating how plasterwork porosity varies with weathering. However, due to the solubility of gypsum in water (0.208 g/100 g at 25 °C [5]), the gypsum void fraction is expected to increase when plasterwork is exposed to humidity (e.g., rain) or humidity rising by capillarity from support elements. It can therefore be concluded that, apart from the amount of water used in plasterwork manufacture, weathering from water also increases its porosity, weakening the material by decreasing its mechanical properties.

3.2. Shore C hardness

Barriac [6] was the first researcher to study the influence of various factors on shore C hardness, concluding that the humidity of plaster and the amount of water used in plasterwork manufacture were the most important factors. He also found that the ratio of shore C surface hardness to w/h was inversely proportional, so the lower the w/h, the greater the hardness, and vice versa. His experimental data gave the following hardness equation (close to linear):

$$H = 127 - 67\frac{w}{h} \quad (3)$$

where H is the shore C hardness and w/h is the water/hemihydrate ratio.

If the shore C hardness is related to the w/h, and the void fraction is also related to the w/h, there must be a relation between the shore C hardness and the void fraction. Combining equations (1) and (2), the following relationship is obtained between these two physical properties:

$$\varphi = \frac{118.45 - H}{152.68 - H} \quad (4)$$

Coquard et al. [7] and Coquard and Boistelle [2] studied the evolution of the hardness of dry and wet plasters as a function of the plaster void fraction, finding an indirect relation between these two properties consisting in the greater the void fraction, the lower the shore C hardness. Unfortunately, neither of the two articles reports the mathematical equation between the two properties.

Table 2
Physical properties of the plasterwork.

Sample	Open porosity (%)	Hardness shore C units
GPD	43.9	77
GPS	47.0	75
GCP	47.6	74
GSF	47.8	75
GSC	48.1	74
GCR	48.2	73
GPS3	49.1	73
GSJ2	49.7	72
GSR	50.9	73
GDR	55.1	71
GPS2	55.5	70
GSE	55.7	67
GCA	56.0	67
GSA	58.1	67
GSJ	58.5	67
GPM	59.0	67

4. Sampling and experimental techniques

We studied a total of 16 samples from 13 plasterwork elements that are the most representative restored and unrestored plasterwork from the Mudéjar period (Fig. 1). Their reference and possible construction materials are indicated in Table 1.

For the physical properties, the surface hardness was determined with a hardness tester model Härtoprüfer, which measures plaster strength to the penetration of a steel needle 0.79 mm in diameter applied with a force of 44.5 N. The results are expressed in the shore C scale (0–100 shore C units) and correspond to an average of twenty assays per sample. The porosity accessible to water was determined according to Standard UNE-EN 1936:07 [8].

5. Results and discussion

5.1. Porosity accessible to water

The open porosity results for the plaster samples are given in Table 2 and they range from 43.9 to 59.0%, which is within the normal range for plaster slurries [2]. In the case of samples GPM, GSJ, and GSA, the porosity indicates a higher ratio of water to plaster than for the others. The aim was probably to produce a slurry with a longer work time due to the difficulty of shaping the floral patterns involved (Fig. 1) or because water was added during the course of the work for the same reason. Sample GCA's porosity (56%) may be attributable to its location outdoors, which makes it more vulnerable to humidity.

The GPD panel has the lowest porosity values, in contrast. It is over 4 cm thick, and it is possible that steps were taken to prevent it from coming loose during work on it. Several compacted layers may have been applied, and the slurry used may have had a low w/h ratio to obtain a dry consistency.

5.2. Shore C hardness

The surface hardness results for the plaster samples are given in Table 2. It can be noted that all the plasterwork has hardnesses that are good or even high, except GSJ, GCA, GSE, GPM, and GSA samples.

These hardness values can provide useful information on the state of conservation of plasterwork because they are related to the void fraction and mechanical strength. To delve further into this point, we studied the statistical ratio between the porosity and

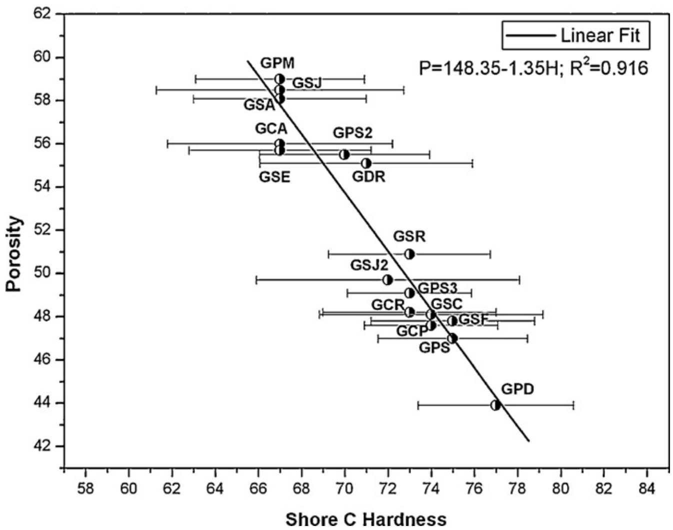

Fig. 2. Graph of porosity versus hardness, including uncertainty hardness range and the regression line.

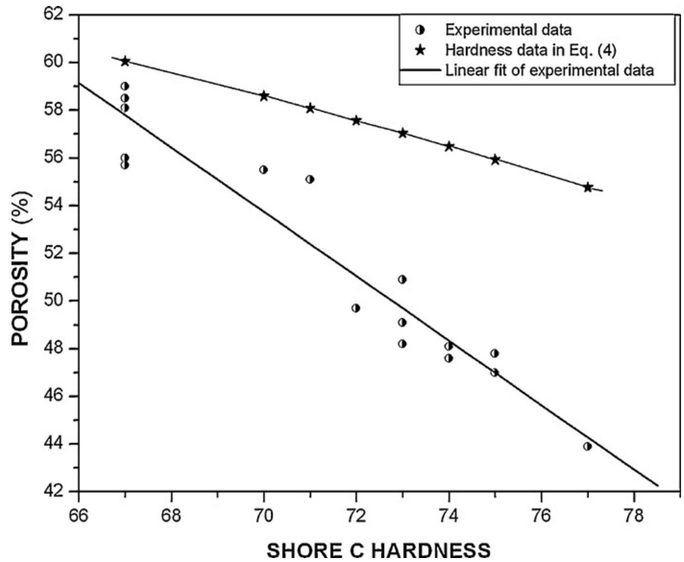

Fig. 3. Graph of porosity versus hardness, including experimental data, their regression line, and hardness data fitting equation (4).

hardness variables for the plasterwork samples (Fig. 2). The linear fit model was chosen from amongst the possible statistical models, it gave a linear regression line as an equation:

$$P = 148.34 - 1.35H \quad (5)$$

where H is the shore C hardness and P is porosity accessible to water (%), the negative slope indicates that the ratio between the two variables is inverse – the greater the hardness, the lower the porosity, and vice versa. The R^2 coefficient of determination was 0.91, indicating that the ratio between the two variables is high but not perfect. The factors that might have affected the coefficient are:

- the samples for the calculation were limited to 16 since that is the number of existing Mudéjar plasterwork;
- the conditions in which the hardness measurements had to be taken on the plasterwork since they are decorative reliefs and have no completely flat surfaces as required by the UNE standard 102-039:85 [9];
- this plasterwork derives from a wide range of periods (14th–16th centuries) and have slight differences in their chemical and mineral compositions, which may affect hardness.

Schiller [4] only indicates that strength is independent of the type of hemihydrate used and not of other minerals or impurities that may be entrained in the hemihydrate.

The results from substituting the hardness values in equation (4) are shown in Fig. 3. Note the significant deviation in porosity estimation given by this equation with respect to the experimental values and how it becomes more acute as the shore C hardness increases. This deviation might be accounted for by the fact that, although Yu and Brouwers [3] and Barriac [6] apply β-hemidrate-based plaster, the contents in β-hemidrate, anhydrite, and impurities are different, and grain size is not specified. The combination of equations (2) and (3) makes mathematical sense, but due to differences in the plaster used, it could cause deviations in the hardness or porosity values.

The practical application of the equation (5) relating porosity to hardness is to determine the porosity via the hardness measurement (shore C durometer), which is indicative of the quality and state of conservation of the plasterwork. The upper limit is 73–79% (void fraction 0.73–0.79) [3,4], at which point the plaster would mechanically collapse.

In the case of the Real Alcázar Mudéjar plasterwork, samples GPM, GSJ, and GSA have the highest porosity and should be subject to regular assessments during the monument's conservation and maintenance program without any future need for sampling.

6. Conclusions

This work has developed a method based on the measurement of the surface hardness (NDT) of the Mudéjar plasterwork (13th–16th centuries) in the Real Alcázar of Seville (Spain). The method provides an estimate of porosity, which property reveals mechanical strength and degree of weathering.

Subsequently, we determined the surface hardness and porosity of the samples and mathematically calculated the equation relating the two properties, finding an acceptable coefficient of determination. Once the correlation is established, it is enough to simply measure the hardness in a specific zone/area of the plasterwork to estimate the porosity without having to remove samples, thereby obtaining valid information on its state and monitoring its conservation. Gypsum porosity, besides being directly related to the w/h used in its manufacture, is also associated with its partial dissolution due to humidity in the weathering process.

Acknowledgments

The authors would like to thank the Real Alcázar of Seville Trust and Center for Research, Technology and Innovation (CITIUS) of the University of Seville for the facilities and collaboration offered during the course of this work. Thanks to Christine Laurin for her translation of the text.

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