Protection and Conservation of the Cultural Heritage of the Mediterranean Cities, Galán and Zezza (eds)

Evaluation of treatments for the stone of the Córdoba Door of Carmona (Seville, Spain)

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ABSTRACT: The Córdoba Door is one of the roman entrances to the old town of Carmona. The Roman part of the monument is built with a calcarenite from quarries near the city. The Door has suffered several interventions in the past, the most important one, dated between 1790 and 1800, is responsible for the exterior structure visible today. The state of conservation of the building has made necessary to restore it. The stone and the rest of building materials are affected by salt crystallization and rising damp. These facts have caused the loss of cohesion of the materials. For these reasons, the application of consolidation treatments, to restore cohesion to the stone, and water repellent treatments, to avoid the water intake, has been considered convenient. As a part of the previous studies for the restoration works, the laboratory evaluation of the behaviour of some treatment products have been carried out.

1 INTRODUCTION

The Córdoba Door of Carmona is situated on the edge of the old town, on an ancient waterway flanked by two borders of the Alcor. It has a roman origin, and its original structure is almost entirely preserved, with two lateral octagonal towers, existing also later works Arab and Christian.

The Door has suffered several interventions; the first recorded information is dated on the XVI century. The exterior structure that is visible today corresponds to a reform made between 1790 and 1800. On Figure 1 a general aspect can be seen.

Figure 1. The Córdoba Door before restoration.

Nowadays a restoration/conservation project has just been finished, due to the high degree of deterioration of the Door. With the aim of carrying out this work taking into account all the information, several investigations have been developed. On a first phase an archaeological study has been made. The second phase consists on the characterization of the materials used on the Door and the determination of their state of conservation. On the third phase, the laboratory evaluation of several conservation treatments has been carried out, in order to select the most appropriate for the monument.

The final aspect of the monument after the restoration works can be seen of Figure 2.

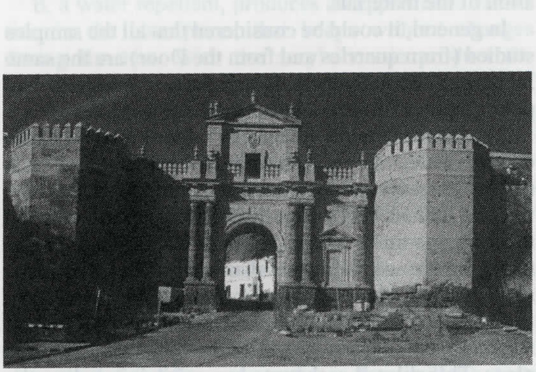

Figure 2. The Córdoba Door after restoration.

Table 1. Average mineralogical composition (%w) of the stone.

Minerals	Qz	Cc	Gp	Dm
Door	23	67	7	Trace
Alcor Q	21	79	Trace	Trace
Batida Q	39	59	Trace	Trace

Qz: quartz; Cc: calcite; Gp: gypsum; Dm: dolomite; Q: quarry.

2 CHARACTERIZATION OF THE STONE

To identify and characterize the stone used, several samples have been taken from the Door as well as from the quarries located close by the city. The identification of the quarries was necessary to use the stone in the restoration. These samples have been analyzed by X-ray diffraction and optical microscopy. A complete description is presented in Espinosa Gaitán et al. (1996).

The average composition of the stone from the Door and from the main quarries is presented on Table 1. These are semiquantitative results obtained from the X-ray diffraction data.

Although with this technique it has not been possible to detect clearly the presence of clay minerals due to their low proportion in these samples, the macroscopic aspect of the stone shows clearly its existence (the rock is very heterogeneus, with macroscopic clay nodules and layers in some areas). By means of aggregated oriented method (which consists in separate the clay fraction) it has been possible to verify that mainly illite and smectite are present among the phylosilicates.

Smectite is an expansive clay that can duplicate its interlayer space easily in presence of water, fact that can explain partially the severe alteration that appears some times. This could be due to disruptive mechanical phenomenon caused by cyclic alternancy of relative humidity on the environment, that produces contractions and dilatations of the structure of smectite. On Figure 3 a detail of the interface between the roman and the neo-classic fabric is seen, as well as the deterioration of the materials.

In general, it could be considered that all the samples studied (from quarries and from the Door) are the same lithotype, although there are slight mineralogical and petrographical differences between the samples.

The stone is mainly formed by a framing of bioclasts of carbonated nature (essentially bivalves, and in a minor quantity bryozoans and nummulites) that are fracture in their major part. These bioclasts are inserted in a fine-grained matrix, also of carbonated nature mainly, although there are also iron oxides and occasionally some clay nodule.

On almost all the samples, the dissolution both of the fine carbonated fraction and of the bioclasts has taken place. This diluted carbonate has reprecipitated on the open spaces of the stone (pores, fissures and original zones of the matrix) in the form of sparitic crystals as

Figure 3. Deterioration of stone on the contact between roman and neo-classic fabrics.

"mosaic". On the samples from the Door, recrystallization inside the stone is more limited, remaining some areas formed practically by the framing of clasts, suffering the stone an increment in porosity and an appreciable loss of compacity.

Besides the carbonated components there is also, with variable proportions (10–20%), a terrigenous fraction formed by quartz grain of different sizes and with rounded and subrounded forms.

It is common for all the samples the presence of gypsum filling some pores, being its abundance variable, but, in general, with higher quantities on the Door samples. This fact suggests that, very probably, this gypsum is intrinsic to the stone, although the high contents found on some samples from the Door indicate that this gypsum could come from joint mortars, some of them having it.

3 LABORATORY TEST TO EVALUATE THE EFFECTIVENESS OF THE TREATMENTS

3.1 *Treated samples preparation*

To prepare the samples, a block fallen down the wall have been cut on cubic samples of 5 × 5 × 5 cm. After cutting, the samples have been cleaned, dried on stove and treated.

The samples have been treated by immersion with the following products:

A. Tegovakon V (Goldschmidt), consolidant based on ethyl silicate.
B. Tegosivin HL 100 (Goldschmidt), organosilicic water-repellent, diluted in white spirit, 5%.
C. Strengthener OH (Wacker), consolidant based on ethyl silicate.
D. ARD 55.050 (Raccanello), acrylsiliconic copolimer, consolidant and water-repellent.

Table 2. Treated samples characteristics.

	W_0 (%)	N_0 (%)	N (%)
Tegovakon	2.20	29.93	27.75
Tegosivin	0.50	32.22	27.74
Stren. OH	2.88	31.83	29.04
ARD	0.93	33.34	30.39

W_0: initial weight; N_0: initial porosity; N: porosity after treatment.

After this, the samples have been let to dry in air, weighed periodically until constant weight. The average values of weight increments, and porosity before and after the application of treatments are presented on Table 2. The weight increments of the samples are proportional to the contents of active matter of the treatments. The porosity has been measured by water saturation under vacuum (Keulen 1972); this method was preferred instead of mercury porosimetry due to the high size of pores.

3.2 *Experimental procedure*

With the aim of evaluating the effectiveness and alterability of the different treatment products in order to select the most appropriate, as well as to reject those that present bad behaviour, a series of characteristics, indicative of the effect that these treatments cause on the stone, have been measured, as well as the response to the weathering factors that act over the building. A methodology similar to those proposed by Aldi (1995), Appolonia (1995) and Caselli (1995) has been followed.

The characteristics that have been measured are: superficial hardness, absorption of water (by capillarity and by immersion) and water desorption.

To simulate the action of these weathering factors in a short period of time, accelerated weathering tests are used. The tests that better reproduce these factors are termohygrometric cycles and salt crystallization.

3.3 *Properties of the samples*

3.3.1 *Superficial hardness*

To determine the effect of the improvement in the cohesion of the material, the mechanical properties are determined, either global or superficial. In this case, this last one has been preferred, since the effect of the treatments is usually manifested in a superficial layer.

The measurement of the superficial hardness is based on the resistance that a material opposes to be penetrated by a harder body. A Rockwell durometer has been used to measure hardness on untreated and treated samples, with a ball of 5 mm, applying a precharge of 10 kg and a total charge of 30 kg. On each sample 27 measurements have been carried out. On Figure 4 the average increments of hardness with respect to untreated stone is represented for each treatment. As it

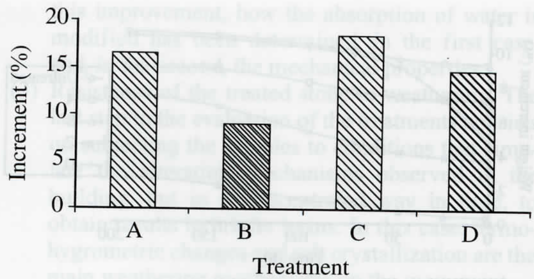

Figure 4. Hardness increment.

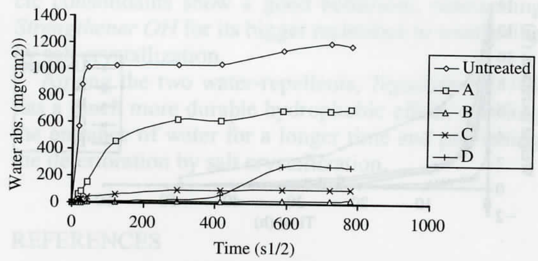

Figure 5. Capillarity water absorption.

can be observed, the increments are higher on the samples treated with the two organosilisic consolidants.

3.3.2 *Absorption of water by capillarity*

The determination of the absorption of water by capillarity has been carried out following the NORMAL (11/85). In Figure 5 the average values of water absorption (expressed as mg/cm^2) are represented in front of the square root of the time (s). The values corresponding to the samples treated with A are very similar to those of non-treated ones, little lesser due to the decrease of porosity caused by the treatments. However, the other organosilicic consolidant, C, has a behaviour more likely a water repellent.

B, a water repellent, produces an appreciable reduction in the absorption, that keeps without changes during the test. With the acrylsiliconic product the hydrorepellency is good at the beginning of the test, but it shows an increment on the absorption later on.

3.3.3 *Immersion water absorption*

The determination of the immersion water absorption has been carried out following the NORMAL (7/81).

In Figure 6 the average values of absorption are represented (weight increment, %) for the samples treated with each product and untreated.

It could be noticed that the hydrophobic effect remains quite well for B. The organosilicic consolidants show the same differences as that in the capillarity test. In this test the contact with the water is much more intense, and the results with D are much worse; the

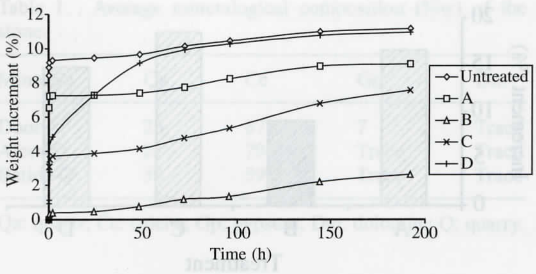

Figure 6. Immersion water absorption.

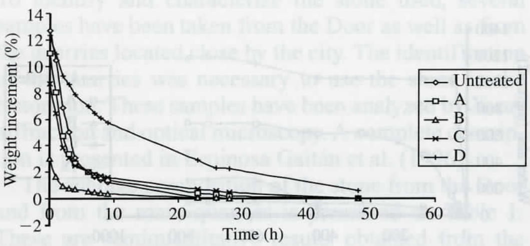

Figure 7. Water desorption.

final absorption has the same value that in the untreated samples, with only small differences in the initial rate of absorption.

3.3.4 *Water desorption rate*

The water desorption rate is determined according to NORMAL 29/88:

– the samples are saturated of water by immersion;
– they are placed in controlled atmosphere with 20°C and 50% of HR;
– they are weighed periodically until constant weight.

The drying curves appear in Figure 7. It is observed that the evaporation process practically does not change with A, B and C, while it diminishes considerably with the acrylsiliconic product. Something similar happens with the critical content, this treatment produces an appreciable increase and the rest does not cause any variation.

These two effects are not desirable, since they make that the stone remains more wet for a longer time, so, all the alteration mechanisms related with water are favoured.

3.4 *Accelerated weathering tests*

3.4.1 *Termohygrometric test*

It consists on subjecting the samples to 20 cycles formed by

– 24 h of immersion in water at ambient temperature;
– 22 h of drying in stove at 80°C;
– 2 h for cooling and weighing.

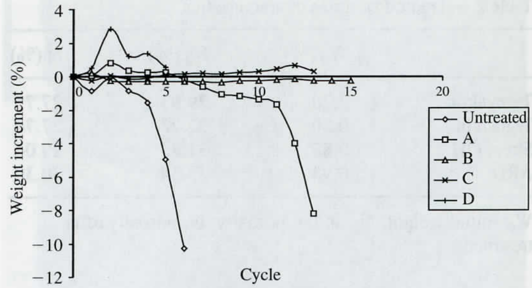

Figure 8. Salt crystallization test.

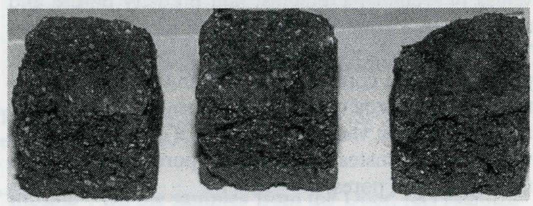

Figure 9. Untreated sample after seven cycles of salt crystallization.

During the test macroscopic alterations have not appeared in the samples, which is confirmed by the weight of the samples, practically constant. For this, no difference between the treatments could be detected.

3.4.2 *Salt crystallization test*

This test, using sodium sulphate diluted at 10%, has been formed by cycles of:

– 24 h of immersion in the solution at ambient temperature;
– 22 h of drying in stove at 65°C;
– 2 h for cooling and weighing.

The control of the weight of the samples is made in each cycle as well as the observation of macroscopic alterations that appear. When the degree of deterioration reached by a sample is high it is eliminated of the test.

In the Figure 8 the average weight evolution (weight increment %) is represented for each treatment during the test.

The untreated samples begin to absorb solution since the first cycle and they begin to loose grains of the surface, until the loss of material is high and the samples finish the test. On Figure 9 the untreated samples are shown after seven cycles.

The samples treated with the organosilicic consolidants have a very similar behaviour to those non-treated, with smaller losses of material, which is indicative of a bigger resistance to the alteration, much higher in the case of C (see Figure 10, samples treated with this product after 12 cycles).

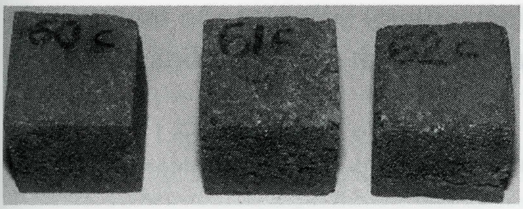

Figure 10. Samples treated with C after 12 cycles of salt crystallization.

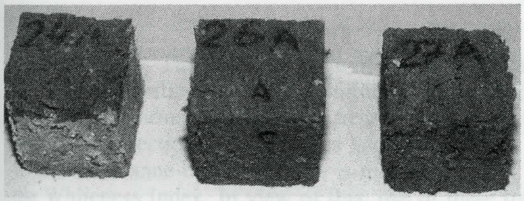

Figure 11. Samples treated with D after five cycles of salt crystallization.

The samples treated with the organosilicic water repellent resist a very high number of cycles without loosing material, which indicates that their hydrophobic properties remain without change.

The samples treated with the acrylsiliconic product show a characteristic behaviour: they begin to absorb solution and to win weight since the first cycle, and the crystallization of the sulphate that takes place behind the treated layer causes the separation and detachment of this superficial layer (see Figure 11).

4 CONCLUSIONS

To evaluate the treatments and to select the best ones, the methodology followed in the IAPH (Villegas 1996) has been applied, studying three aspects:

(1) Compatibility of the treatment with the material. To determine if a treatment is acceptable, it is fundamental to know how it modifies some characteristics of the material (colour, porosity, permeability, and water drying rate). If the variation caused is excessively high, it could be necessary to discard the treatment.
(2) Effectiveness of the treatment. Treatments are applied with the object of getting an improvement in certain characteristic. In the case of the water-repellent products, to diminish the entrance of water in the stone; in the case of the consolidants, to increase the cohesion of the material. To evaluate this improvement, how the absorption of water is modified has been determined, in the first case, and, in the second, the mechanical properties.
(3) Resistance of the treated stone to weathering. The last step in the evaluation of the treatments consists on subjecting the samples to conditions that simulate the alteration mechanisms observed in the building, but in a concentrated way in time, to obtain results in briefer terms. In this case, termo-hygrometric changes and salt crystallization are the main weathering mechanisms on the monument.

With this methodology, it is possible to determine which treatments have better behaviour. Both organosilicic consolidants show a good behaviour, outstanding *Strengthener OH* for its bigger resistance to weathering by salt crystallization.

Among the two water-repellents, *Tegosivin HL 100* has a much more durable hydrophobic effect, avoiding the entrance of water for a longer time and preventing the deterioration by salt crystallization.

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