12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

EVALUATION OF CONSERVATION TREATMENTS APPLIED TO THE STONE OF THE CATHEDRAL OF JEREZ DE LA FRONTERA (CÁDIZ, SPAIN)

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Abstract

To carry out an appropriate intervention in a very important building, the Cathedral of Jerez de la Frontera (Spain), it is necessary to make a careful characterization of the materials used and to determine the weathering factors and mechanisms that are affecting this building. In order to select the treatment products to be applied, it has to be studied their influence on the properties of the materials and also the behavior of treated materials in a long term.

In previous papers the characterization of materials used in the construction of the Cathedral and the deterioration mechanisms present in it were described. In this paper we show the results of the evaluation of several conservation treatments applied on stone samples from the building and from the quarry which provided the stone used in the construction of the building.

The treatments were: Estel 1000 (consolidant), Silo 111 (Water repellent), Estel 1100 (both effects). It has also been tested the combination of Estel 1000 and Silo 111.

To evaluate the performance of treatments on the stone samples, several material properties have been measured, such as porosity (vacuum water absorption), water desorption rate, color, ultrasound transmission velocity, capillary water absorption. Finally, the behavior of treated and untreated samples in the presence of soluble salts (one of the main weathering factors), has been determined by mean of a salt crystallization test.

Keywords: calcarenite stone, durability, consolidant, water repellent, salt crystallization test.

1. Introduction

Jerez Cathedral is a seventeenth century building; in particular, its construction was developed between 1695 and 1778. The cathedral was built originally as a Collegiate Church, raised over the original Great Mosque of Jerez and the ancient Church of the Saviour, whose origin dates from 1264 (Ríos, 1980).

In the late seventeenth century, the old Collegiate Church of Jerez was ruined so the City College and the City Council decided to demolish it to build a new one. This work began on 1695 under the direction of Diego Moreno Meléndez (Javierre, 1979). After several interruptions, on 1778 the inauguration of the new church was celebrated, although works continued until 1849 (Repetto, 1978).

The construction works of the temple lasted over more than eighty years. This long duration causes that three architectural styles can be found on the Cathedral: neoclassical, Baroque and Gothic (Repetto, 1978).

This work includes, as the main objective, the study of the conservation state of the stone from the Cathedral, the identification of main weathering causes and the proposal and evaluation of possible conservation treatments. The methodology applied consists of the following phases:

- Diagnosis of alteration of the materials from the Cathedral, which includes the characterization of stone materials of the temple as well as the identification of visual deterioration indicators.
- Study of weathering agents: study of the environmental parameters and former interventions that have been able to influence on present state of the stone.
- Determination of the effectiveness of conservation treatments (consolidants and water repellents) on the stone by means of laboratory tests with stone samples.
- Proposal of conservation measures taking into account the results obtained in the previous section in order to contribute to better conservation of the temple.

2. Material and methods

2.1 Stone type

The stone of Puerto de Santa María (PSM) is the predominant lithotype that can be found at the Cathedral of Jerez. It is an ivory colored bioesparithic calcarenite, with an average open porosity of 35% (Villegas, 1989). It is a soft, crumbly rock, to the point that the grains can be detached by simple friction. Macroporosity is predominant, while the microporosity is practically inexistent and medium-sized pores scarce.

Chemical characterization

A parameter that can provide essential information in the study of these stone materials is their chemical composition. Through various chemical methods, Rodriguez Sanchís (1998) obtained the main elements of lithotype, presented in the table 1.

Table 1. Main elements of the PSM lithotype

	LOI	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
PSM	26,30	39,41	0,28	0,27	33,09	0,15	0,39	0,18	0,28

Weathering factors and indicators

The weathering factors are defined as parameters capable of inducing negative changes in certain properties of the stone, considered as building material, changes that become evident as weathering indicators. Following the terminological recommendations of Alcalde (2003), we can summarized as indicated bellow.

In the case of the stone of the Cathedral, the main weathering factors that affect it are: wind, thermo-hygrometric oscillations, soluble salts and biological agents.

In the province of Cadiz, the most representative climatic factor is the wind, that plays an important role in the alteration of the stone. It causes, mainly: increased water evaporation rate, erosion, contribution to the marine salts intake and enhancement of the rainwater penetration.

The high air humidity produces high water content on the stones, which will participate in various forms of alteration such as crusts, efflorescence, pitting, concretion, incrustation, alveolar erosion, grain disaggregation, peeling, grinding, swelling, etc.

The thermal factors will mainly produce breaks (fracture, cracking and fragmentation), contour scaling, warping and swelling.

The presence of salts causes the following weathering indicators: efflorescence, crusts, chromatic alteration, concretion, striction, pitting, crater formation, corrosion, alveolar erosion, swelling, blistering, contour scaling, peeling, chipping and film separation.

As biological agents, it can be included from microorganisms to plants and animals, and the most common indicators that produce are deposits, spotting, disaggregation and pitting.

Although there are evidences of materials deterioration all over the temple, the facades that present the most important signs of alteration are the main (N-NW) and western ones while the southern has suffered lack of maintenance. The dome and the upper terrace sculptures are in good condition, probably due to the application of conservation treatments in the past.

The magnitude of the main weathering indicators in the inner part of the temple is shown on table 2 (Rodriguez Sanchís, 1998).

Table 2. Qualitative magnitude of weathering indicators of the building

Weathering Indicators	**Importance**
Chromatic Alterations	++
Material losses	+++
Cracking	+++
Incrustations	+
Plants	++

+ Low ++ Medium +++ High

2.2 Samples preparation

Cubic samples of 5cm have been prepared from blocks taking from the original quarry (in Puerto de Santa María), and from ashlar fragments from the cathedral. After cutting, the samples have been cleaned, dried to the air till constant weight. In this way, the stone has got and hygroscopic water content in equilibrium with ambient.

The treatments characteristics are summarized on Table 3. Estel 1000 is a consolidant product, Estel 1100 is consolidant and also water repellent and Silo 111 is a water repellent.

Table 3. Treatments characteristics

Product	**Manufacturer**	**Properties**	**Dilution**	**Composition**
Estel1000	CTS S.r.l.	Consolidant	75% on white spirit	Tetra ethyl silicate
Estel 1100	CTS S.r.l.	Consolidant + Water repellent	75% on white spirit	Tetra ethyl silicate + Oligomeric polisiloxane
Silo 111	CTS S.r.l.	Water repellent	10% on white spirit	Oligomeric organosiloxane

To get an impregnation as uniform as possible, the samples have been treated by immersion in the products during ten minutes, time enough, due to the high porosity of stone, to get a complete impregnation. The treatments drying process has been followed by weighing the samples daily until constant weight. In table 4, the weight increments due to conservation products applications are shown. Before and after the treatment, the total open porosity (Ontiveros, 1998) of all the samples have been measured (Figures 1and 2).

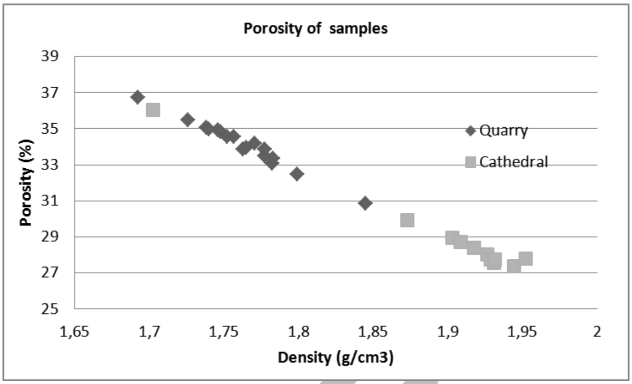

Figure 1. Porosity / density of samples

On figure 1 it can be see the inverse linear relation between porosity and density of both types of samples, showing that density and porosity of all of them keep the same relation.

Table 4. Weight increment (%) of samples after products applications

Product	**Weight increment of samples from quarry (%)**	**Weight incr. of samples from the Cathedral (%)**
E1000	6.25	5.60
E1100	5.57	4.92
S111	0.58	0.57
E1000 +S111	5.64	5.21

Weight increments are lower on cathedral samples, accordingly with their lower porosity and lower absorption of treatments.

The application of Silo 111 after Estel 1000 has been carried out after 20 days of drying of the first impregnation. Although in this period of time Estel 1000 was supposed to be completely dried, the weight increment with both products is lower than those obtained only with Estel 1000, so probably the partial dissolution of the consolidant deposited on the stone has taken place, indicating that the product was not completely polymerized and more drying time was needed. It´s important to take this fact into account to develop properly the *in situ* application of treatments.

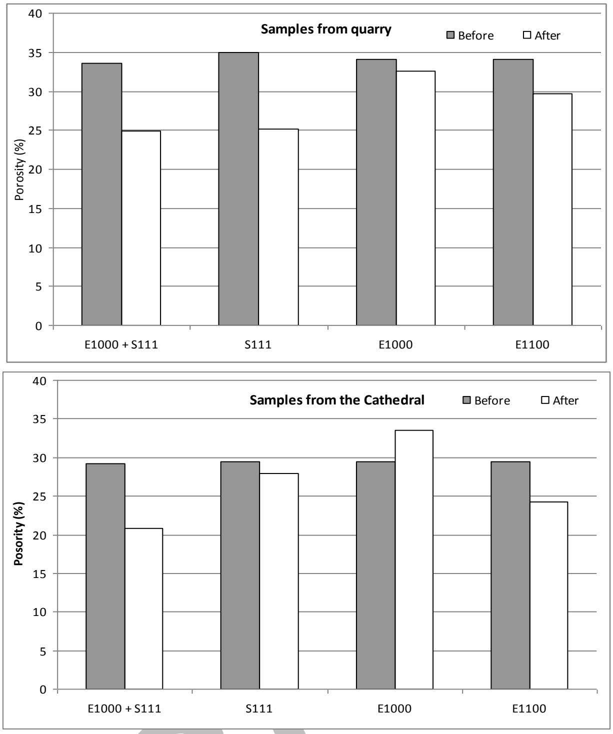

Figure 2. Open porosity (%) of samples before and after impregnation. Average values of five samples

The samples from the Cathedral have lower porosity, fact that could seem not logical, taking into account the alteration of the building stone. This is probably due to the high variability of this stone, coming from a very big quarry, which has been in use since the late 14th century.

All the treatments produce a decrement on porosity and, on both types of stone, the higher change is caused by the combination of E1000+S111.

2.3 Experimental procedure

To evaluate the effectiveness and alterability of the different products and to select the most appropriate, as well as to reject those that may present a bad behaviour, several characteristics indicative of the effect that these treatments could produce on the stone have been measured. The response of the treated samples to the weathering factors that act over the Cathedral of Jerez has been determined by means of an accelerated weathering test.

The characteristics that have been determined are: colour, ultrasonic velocity, water absorption by capillarity and water desorption. The accelerated test has been a salt crystallization one, using a sodium sulphate solution at 10%.

3. Results

3.1 Hygric properties

Capillarity absorption has been determined on all the samples, following the test proposed by Ontiveros (1998), adapted from UNI-EN-1925. On figure 3 it is represented the weight increment (water absorbed) versus the square root of time. The amount of water absorbed by untreated samples is quite different for weathered (Cathedral) and unaltered (quarry) stone, with a difference of 4% with respect to sample weight.

The treated samples of both types of stone have a similar behaviour. Estel 1000 shows a slower absorption, especially at the first part of the test, and the final weight increment is the same for both types, about 11%. Silo 111, when applied alone, protect quite well from the entrance of water, with less than 1% of absorption. Not so good is the result when it is applied after Estel 1000, being better on the quarry samples, 1.3 % than on the cathedral samples, 2.7 %. Estel 1100 does not act so effectively as water repellent, with an absorption of 5.2-5.6 %.

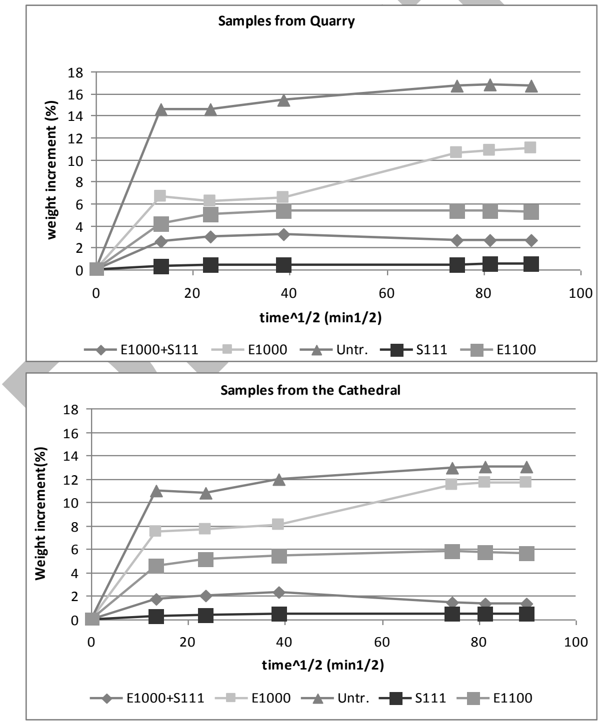

Figure 3. Capillarity absorption. Average values of five samples

Water desorption for all samples was measured and results are shown in Figure 4 and Table 5 (NORMAL 29/88).

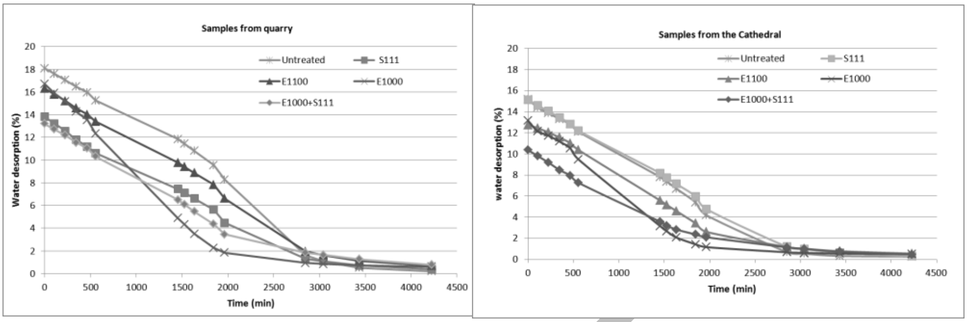

Figure 4. Water desorption. Average values of five samples

Table 5. Water desorption rate (water content (%)·min^{-1})

Product	**Samples from Quarry**	**Samples from Cathedral**
Untreated	0,0044	0,0051
S111	0,0042	0,0049
E1100	0,0045	0,0052
E1000	0,0081	0,0067
E1000+S111	0,0047	0,0044

The treatments do not produce decrement in the initial drying rate, even Estel 1000 makes this process quicker. The final water content reaches very similar values for all treatments, so it can be said that the effect of the treatments over the water movement inside the stone is almost inappreciable.

3.2 Cohesion of stone

The cohesion of the stone has been determined indirectly through the ultrasonic rate (Ontiveros, 2000). It has been measured in the three perpendicular directions, and average values are shown in Figure 5.

The ultrasonic velocity is higher on the cathedral samples, accordingly with its lower porosity. Although, the effect of the treatments is contrary on both stones: while the ultrasonic velocity is incremented on quarry samples, on the cathedral ones the result is quite unexpected, diminishing with all of the treatments.

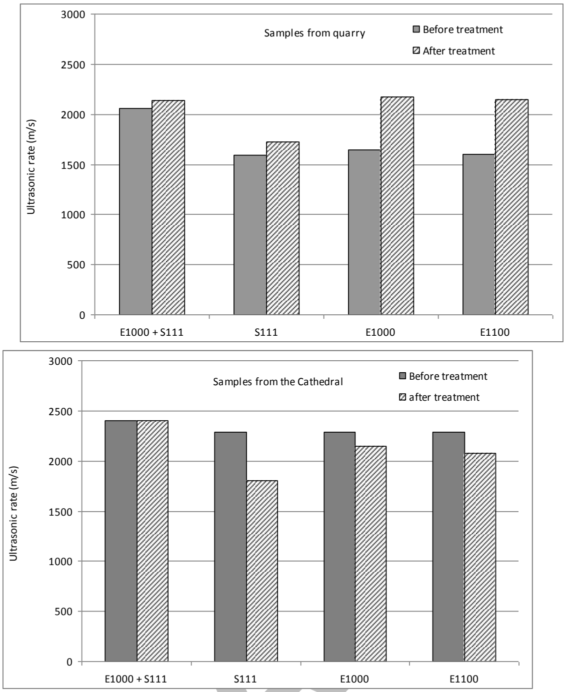

Figure 5. Ultrasonic velocity. Average values of five samples

3.3 Colour

The colour of samples before and after treatments application was measured using a Colorimeter Minolta CR-210 and using templates for diameter reduction according to Arroyo et al (2008).

The application of both E1000 and E1100 affects slightly to the colour of both stones, with ΔE ranging bettween 2-3. Silo 111 affects clearly to quarry samples, with ΔE of 6.2, while the combination of E1000+S111 induces similar changes on both stones, around 5 (Figure 6).

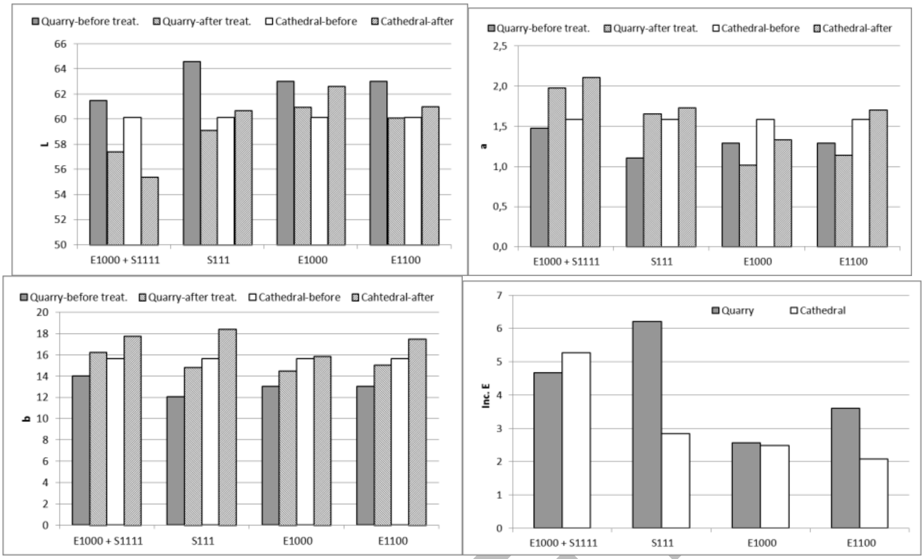

Figure 6. Colour before and after treatment applications. ΔE due to treatments. Average of five samples

3.4 Salt crystallization test

The test carried out is that proposed by Villegas (2000), adapted from UNI-EN-12370. A 10% sodium sulphate solution is used and it is formed by 20 cycles as follows:

24 hours of immersion in the solution
22 hours of drying at 65ºC
2 hours for cooling and weighing

This rock has a great proportion of macropores, so it resists quite well the effect of salt crystallization/hydration. For this reason, in general the samples do not develop important alteration during the test.

Untreated samples began to lose material after ten cycles, with an average weight loss of 1%. The deterioration consists on the fall of grains homogeneously from all the surface. The same behaviour is shown by samples treated with Estel 1000 and Estel 1100, but in these cases grain fall began after 15 cycles and weight losses are smaller than 1%. When Silo 111 is applied with Estel 1000, the situation is better than with the consolidant alone, and samples weight remains almost unchanged. Silo 111 alone gives the best protection to the stone, and negligible changes took place.

4. Conclusions

A qualitative assessment to each treatment on each test was assigned, obtaining in this way a global view of the response of the stone. This valuation allows the selection of the best treatment for the restoration of the cathedral.

Table 6. Global evaluation of treatments

	E1000+S111	S111	E1100	E1000
Weight increment	+	+	+	++
Porosity variation	-	++	+	++
Capillarity absorption	+	++	-	0
Water desorption	-	0	0	++
US rate	0	-	-	0
Colour changes	-	0	+	0
Accelerated weathering	++	++	+	+

++ the best *+ good* *0 indiferent* *- negative*

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