

COMPARATIVE ANALYSIS FOR THE ASSESSMENT OF RESTORATION TREATMENTS ON STONE MATERIAL FROM THE ROMAN THEATER OF MERIDA (SPAIN)

N. Perez-Ema^{1,4,5}, MF. Alberghina², D. Fontana², A. Longo², M. Marrale², L. Tranchina³, M. Brai^{2,3}, R. Bustamante⁴, M. Alvarez de Buergo⁵

¹ CEI Campus Moncloa. UCM-UPM. Edif. Real Jardín Botánico Alfonso XIII, Avda. Complutense, s/n 28040 Madrid.

² Dipartimento di Fisica e Chimica – Università degli Studi di Palermo – Viale delle Scienze, Ed. 18, 90128 Palermo

³ Laboratorio di Fisica e Tecnologie Relative - UniNetLab – Università degli Studi di Palermo – Viale delle Scienze, Ed. 18, 90128 Palermo

⁴ Escuela Tecnica Superior de Arquitectura, Universidad Politecnica de Madrid. Avda. Juan de Herrera, 4. 28040 Madrid, Spain.

⁵ Instituto de Geociencias, IGEO (CSIC, UCM). C/ José Antonio Novais, 2. 28040 Madrid.

The work described arises from the collaboration between different research groups, under the framework of the PICATA programme (CEI Campus Moncloa):

- AIPA research group (ETSAM, UPM),
- Institute of Geosciences, IGEO (CSIC, UCM),
- Laboratorio di Fisica e Tecnologie Relative- UniNetLab (UNIPA).

The overall goal of the project is the study of effects of conservation treatments applied on stone material from archaeological sites, in terms of superficial changes, effectiveness and durability. In this sense, one of the first premises is characterize the surface of the treated and untreated material in order to determine changes in physical and chemical properties.

Emerita Augusta (Merida) is a Roman archaeological city listed by UNESCO in 1993, where the Theater is the most representative monument of the whole ensemble (Figure 1).



Fig.1: Overview of the Roman Theater in Merida (Spain)

This study explores the use of non-destructive techniques for the evaluation of stone samples, with and without different protective/consolidating products. In particular, samples of marble

and granite from the Front Stage of the Roman Theatre (Figure 2), material present in many other remains of the city, due to the proximity of the quarries [1].



Fig.2: Marble and granite samples: (S) samples treated with Ethyl Silicate, (H) samples with a hydrophobic product, (S+H) samples with both treatments, and (N) non-treated samples.

Methodology

Comparative analysis focuses; on the one hand, in chemical study for the detection and characterization of treated and untreated surface. Methodology and techniques used for that purpose are the following:

- ✓ X-ray fluorescence-XRF, in order to evaluate the elemental composition differences between treated and untreated samples.
- ✓ Laser-Induced Breakdown Spectroscopy-LIBS, to reveal chemical elements not detectable by XRF and also to analyse the stratigraphic sequence of different layers starting from the treated surface up to the bulk [2,3].

On the other hand we studied the differential hydric behaviour of samples, in order to evaluate the protective efficacy of these products:

- ✓ Nuclear Magnetic Resonance-NMR for the comprehension of changes regarding the distribution of water in the porous structure [4].
- ✓ Mercury Intrusion Porosimetry, allow as also to check changes in the porous system.

Methodology followed allowed us, in addition, to check advantages and limitations of each technique, and its suitability for assessing the effects of treatments.

Results and Conclusions

XRF measurements allow us to reveal the presence of treatment by monitoring the presence of Silica (Si) marker. Results confirm that the amount of Si varies increasingly when comparing treated and untreated samples, being purely clear only when confronted with S+H, and moderately distinguishable between untreated, and treated with S or H (Table 1).

Samples	Non-treated	Treated with Ethyl Silicate (S)	Treated with hydrophobic (H)	Treated with both products (S+H)
Si	1140.1	1185.9	1617.0	6372.5

Table 1: Average net area of silica picks for white marble samples comparing treated and untreated samples

Presence of Si also varies when comparing different faces of the same sample, thus, more Si is detected in exposed/weathered faces, and less in fresh (recently cut) faces. That is due to the presence of Si in deposits of external surfaces (Table 2).

Samples	Non-treated	Treated with Ethyl Silicate (S)	Treated with hydrophobic (H)	Treated with both products (S+H)
Si exposed face	1969.0	2373.9	3119.0	6419.3
Si cut face	27.8	558.2	886.6	4744.4

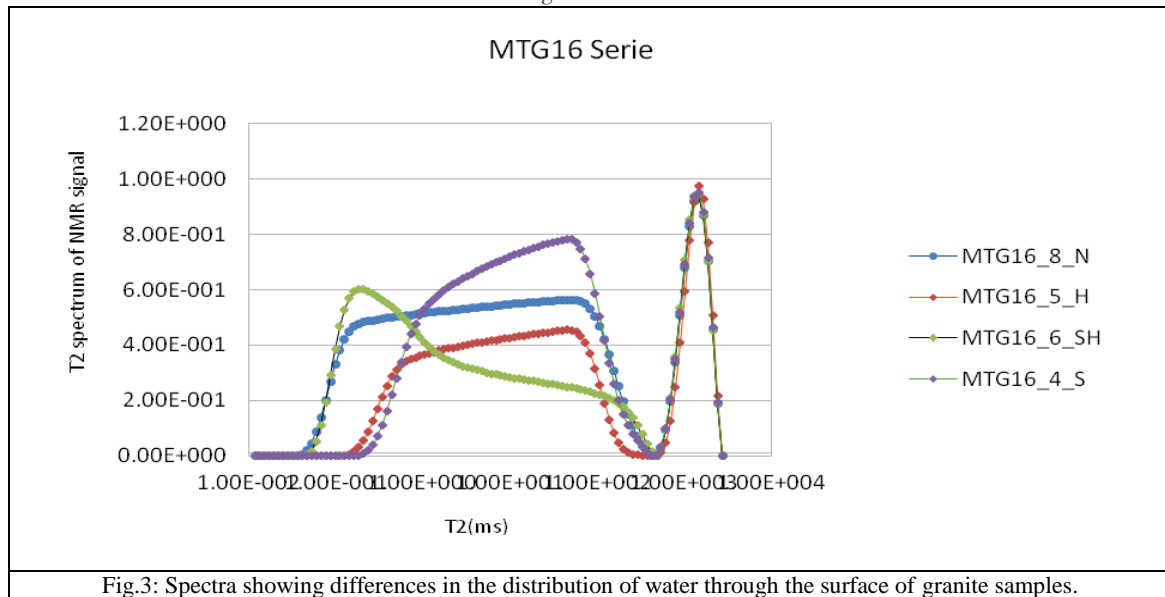
Table 2: Average net area of silica picks for white marble samples comparing exposed and non exposed faces

Nonetheless, it can be concluded that, despite having silica in the exposed surface (and therefore closer to real on site conditions), increasing of Si is distinguishable also between treated and untreated samples, but been only unmistakable in the case of S+H. However, when this comparison is made over recently cut faces the differences in Si content become much clearer, been possible to distinguish between the three different treatments and the untreated samples.

LIBS measurements confirm what XRF showed, presenting higher presence of Si on treated surface. In addition, the Si content decreases as deepens the surface layer (sequence up to 15 shots).

Finally, NMR measurements, although showing more heterogeneous outcomes, allow observing some changes in the balance between micro-, mid- and macro-porosity. It also shows a tendency to homogenize the distribution of water in the pore system in samples treated with a hydrophobic product, thus, the water gets all kinds of pores, while in the untreated sample it is mainly located in micro-pores.

A general review of NMR spectra shows exceptional changes in the distribution of water in the pore system by the effect of the different treatments (Figure 3). In contrast, Porosimetry Hg tests show an overall decline of the porosity (from a 3.84% in untreated samples to a 0.21% in treated with S+H in MTM27 samples) as well as a shift in the balance between micro and macro-porosity, favouring the first one in the case of granites.



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