CALCIUM HYDROXIDE NANOPARTICLES IN CULTURAL HERITAGE CONSERVATION

EVALUATION OF THE EFFECTIVENESS IN LASPRA DOLOSTONE

Aránzazu SIERRA-FERNÁNDEZ[1]*, Xavier MAS-BARBERÀ[2], Julia OSCA-PONS[3] and Stephan KRÖNER[4]

[1] Instituto de Geociencias (CSIC-UCM), Madrid, Spain

[2,3,4] Institut Universitari de Restauració del Patrimoni, UPV-Valencia, Spain

The main aim of the present work has been to evaluate the effectiveness and stability of the calcium hydroxide nanoparticles dispersed in alcohols applied to dolostone (Laspra, Asturian dolostone, Spain), in relation to some typical problems to the *in-situ* and real application

1 INTRODUCTION

The appearance of nanolimes represents a progress in the use of the calcium hydroxide as an inorganic consolidant of stone heritage since the effect of particle size reduction, certain properties can be improved [1]. However, it is fundamental to study the compatibility of the $Ca(OH)_2$ nanoparticles with the stone material type, as well as their effectiveness addressing various problems such as the penetration depth of the consolidant, the presence of salts in the material, the solution concentration and the environmental conditions of application [2, 3]. The research has been focused on a chapiter of Laspra dolostone, conserved in the Archeological Museum of Asturias, treated with $Ca(OH)_2$ nanoparticles and in which no positive consolidation results were obtained.

2 EXPERIMENTAL

MATERIALS

STONE MATERIAL

Twelve cubic specimens of Laspra dolostone (Asturias, Spain) of 5 cm side were used in this study. Laspra is a micrite composed mainly of dolomite (90%) and characterized by its high open porosity (around 30%). In order to assess the behavior of nanoparticles applied to the stone substrate containing a certain amount of salts, six of the twelve specimens were subjected to a desalination process using a water bath desalination method.

CONSOLIDATING PRODUCT

The product used was a colloidal suspension of nanoparticles of calcium hydroxide dispersed in isopropyl alcohol, distributed commercially under the name of Nanorestore®.

METHODOLOGY

APPLICATION OF CONSOLIDATING PRODUCT

Dolostone specimens were treated in a climatic chamber at 20ºC and 90%RH to simulate the conditions in which the nanoparticles were applied to the piece under study. The consolidating product was applied by brushing. These applications were the same as the ones applied to the chapiter and were achieved in nine and ten sessions that were separated one from another for five days. Furthermore, in one part of the specimens, the employment of the product was conducted with the exception of the last application (Table 1).

ANALYTICAL TECHNIQUES

Optical microscopy (OM): used for studying the porous structure and cohesion degree of the material stones, using a DMR Leica optical microscope.

Scanning Electron Microscopy coupled with Energy dispersive X-rays analysis (SEM-EDX): used for the characterization of the samples, the reached penetration depth of the treatment and the interaction between the product and the stone substrates. This study was carried out using a Jeol JSM 6300 Scanning Electron Microscope operating with a Link-Oxford-Isis microanalysis system. The analytical conditions were: 20 kV accelerating voltage, 2 x 10^{-9} beam current and 15 mm as working distance.

X-rays diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR): used for the determining of the carbonation degree. The XRD data were collected by means of a BRUKER AXS D5005 diffractometer, over the 2θ range of 5- 80° at a count time of 0.8 s. The infrared spectra were obtained using a Vertex 70 (Bruker Optics). The number of co-added scans was 32 at a resolution of 4 cm^{-1}.

Table 1

Specimens	Treatment	Salt content	Environmental conditions
L1, L2, L3	Treatment 1	Without desalting	T:20ºC; RH:90%
L4, L5, L6	Treatment 1	Desalinated	T:20ºC; RH:90%
L7, L8, L9	Treatment 2	Without desalting	T:20ºC; RH:90%
L10, L11, L12	Treatment 2	Desalinated	T:20ºC; RH:90%

Treatment 1.
5 applications of nanoparticles diluted in isopropyl alcohol in a concentration of 1.25 g/l
4 applications in a concentration of 2.50 g/l
1 application in a concentration of 5.0 g/l

Treatment 2.
5 applications of nanoparticles diluted in isopropyl alcohol in a concentration of 1.25 g/l
4 applications in a concentration of 2.50 g/l

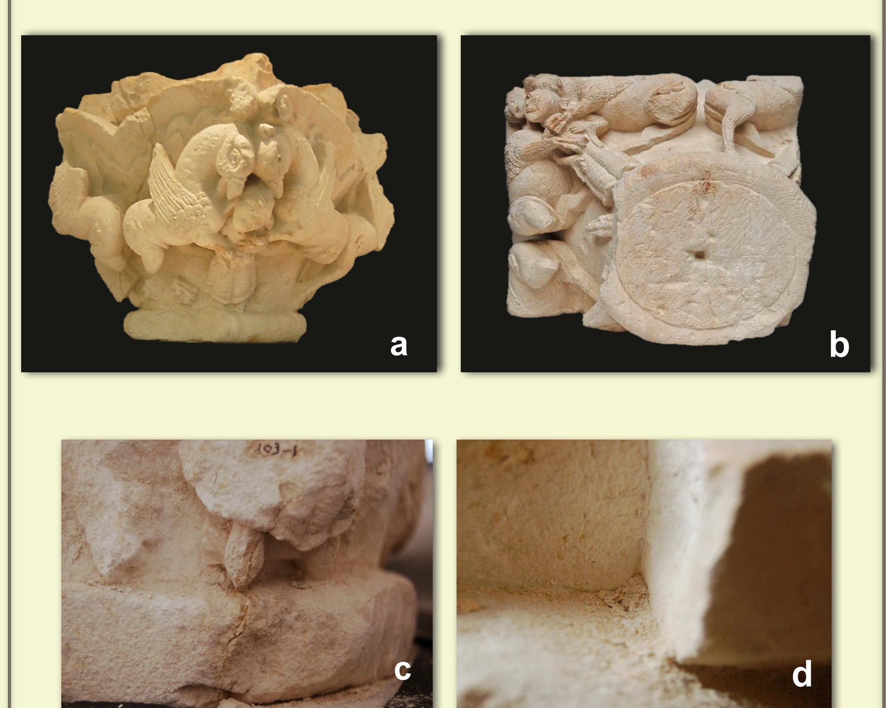

Fig. 1. (a) and (b). Views of the chapiter. Dimensions: 29 x 42 x 37 cm; (c) and (d). Detail of the conservation status of the chapiter.

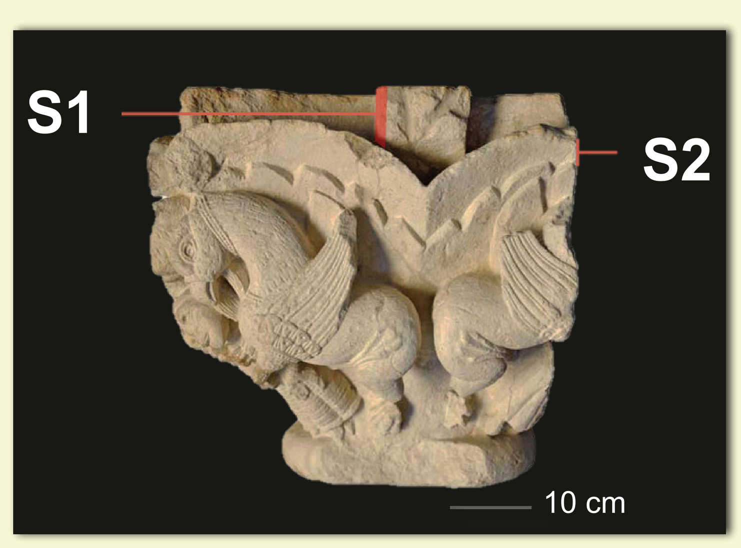

Fig. 2. Right side of the chapiter. Sampling sites

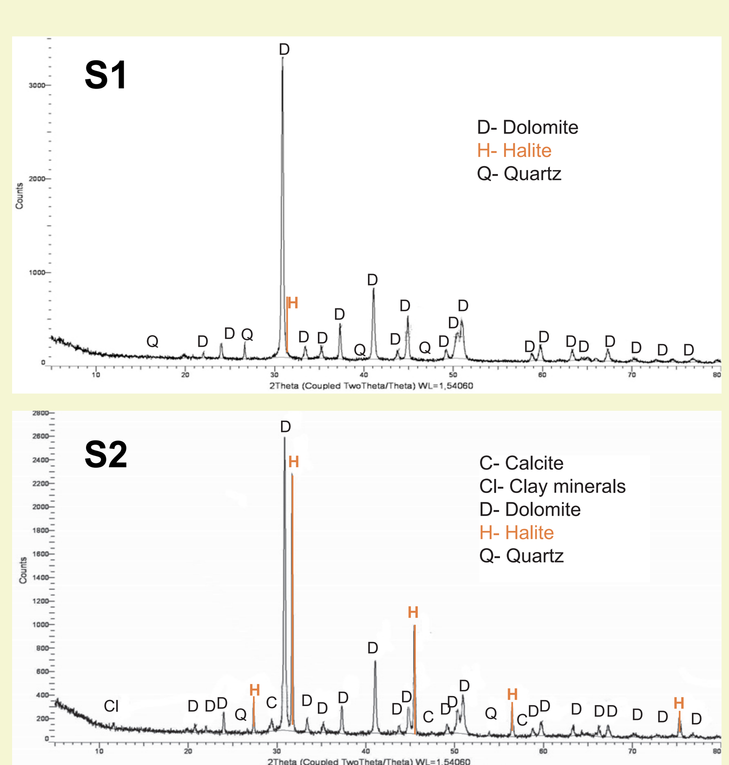

Fig. 3. X-ray diffractograms obtained in the samples "S1" and "S2". This results confirmed the presence of soluble salts in the chapiter.

3 RESULTS

SEM-EDX analysis revealed that the treatment reached a **penetration depth** of about **0.5 cm** in the **desalinated** specimens and of **1 cm** in the specimens **without desalting**. In addition, the EDX element distribution maps of the elements calcium (Ca) and magnesium (Mg), allowed to appreciate a different consolidant performance in surface, according to the content of salts in the stone. The surface of **the desalinated stone material presented greater progress of carbonation** of the nanomaterial by filling the substrate porosity.

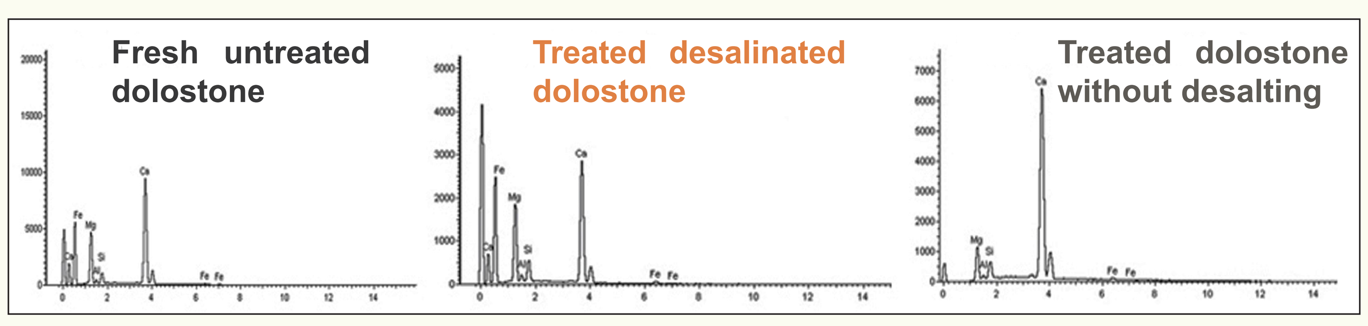

Fig. 4. EDX spectra obtained of the internal cross-sections of the samples at depth of 1cm

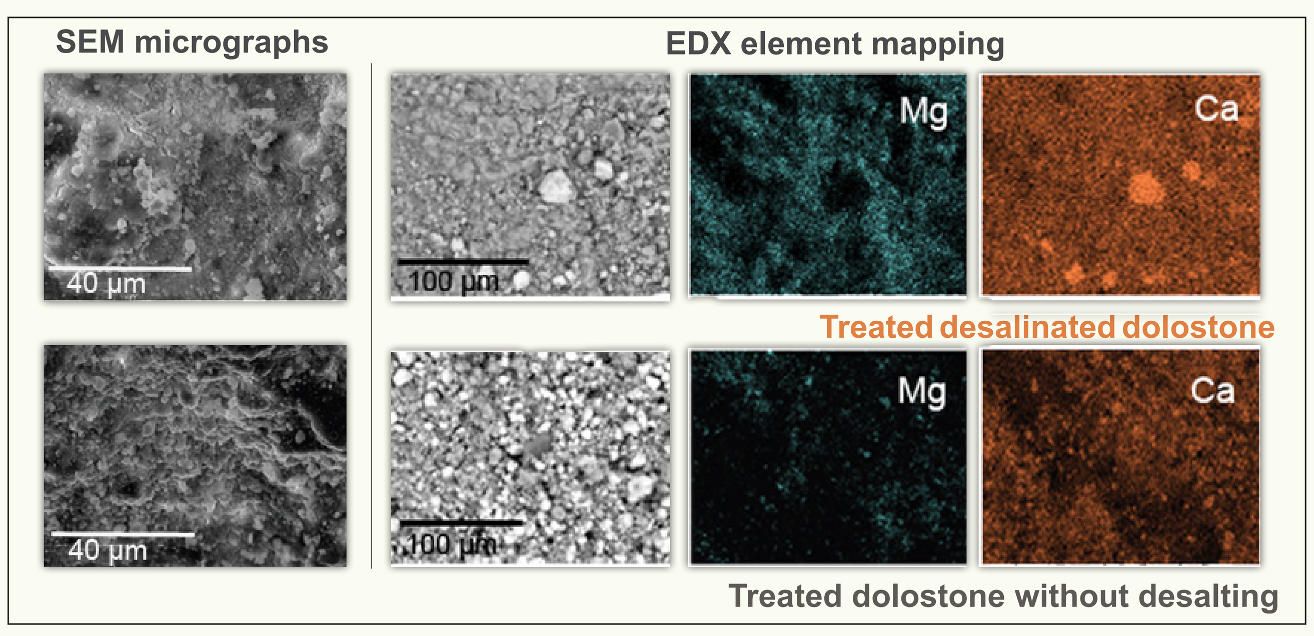

Fig. 5. SEM images, 1500X and the distribution of elements obtained by EDX element mapping

The data obtained by SEM/EDX on **the treated specimens without the last application of $Ca(OH)_2$ nanoparticles** showed more progress in the reaction of carbonation of the consolidating product. The application of the more diluted nanoparticles solutions improved the degree of penetration of the nanomaterial.

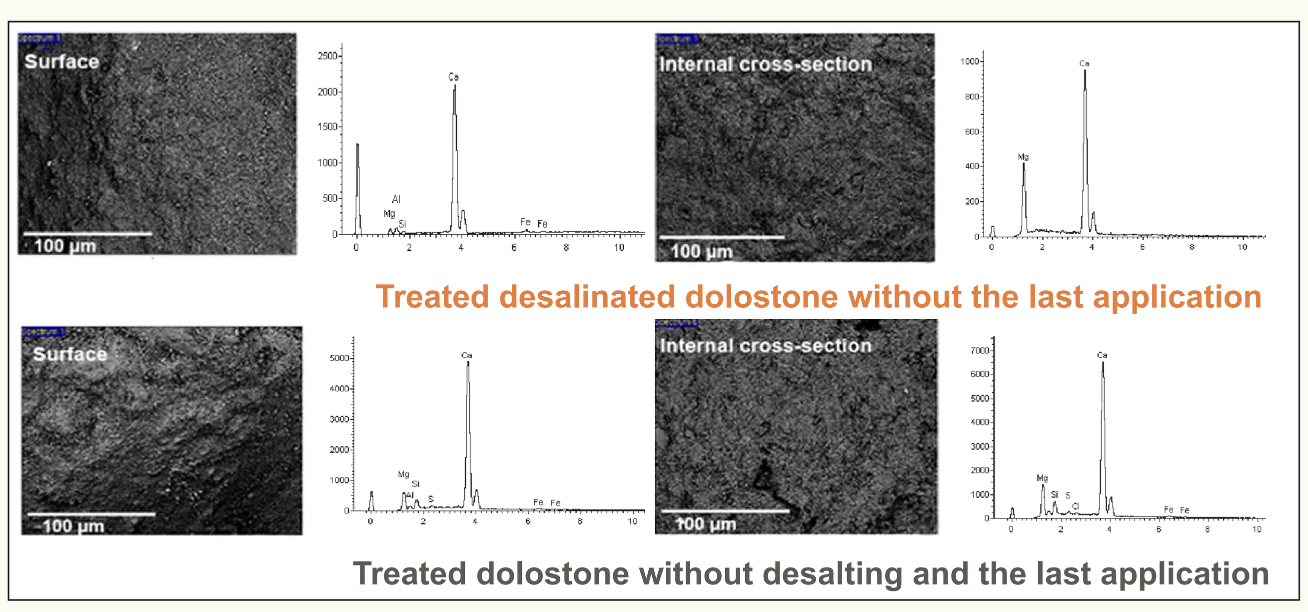

Fig. 6. SEM images, 100X and the EDX spectra obtained

The analysis carried out after five months of treatment in all specimens confirmed **a complete carbonation** of $Ca(OH)_2$ nanoparticles. All the test specimens showed that the dolomite ($CaMg(CO_3)_2$): IR absorption bands in the range of 1404, 876 and 727 cm^{-1}, was the major mineral phase. These data were in accordance with previously results obtained by XRD.

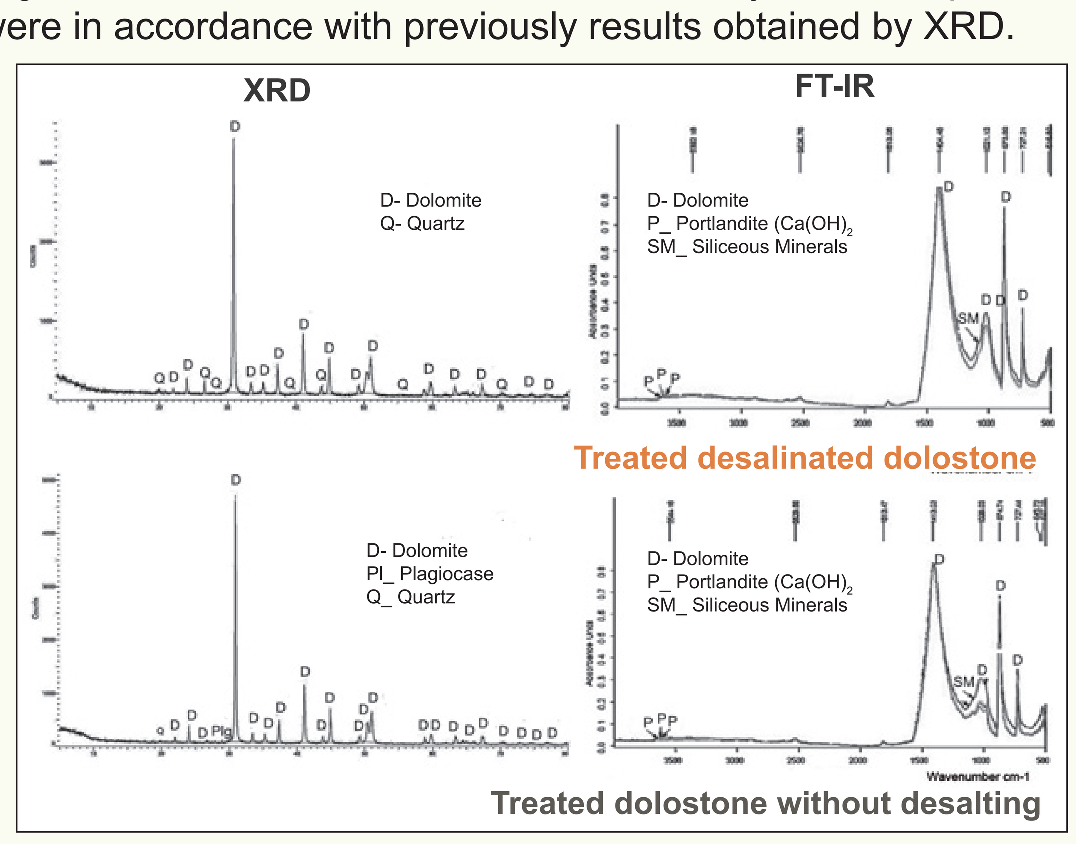

Fig. 7. XRD diffractograms and FTIR spectra of treated specimens, after five months

4 CONCLUSIONS

The effectiveness of the $Ca(OH)_2$ nanoparticles is conditioned by the relative humidity in which the consolidation is carried out. The dolostone treated to a high humidity (90%RH) experienced, after treatment, a very high increase of residual moisture from the carbonation of the consolidant under this conditions. This caused the consolidant efficacy to decrease.

The presence of soluble salts into the stone material inhibits the action of the nanoparticles. This fact slowed down its carbonation rate significantly, encouraging a greater penetration depth (1 cm) of the nanomaterial in the stone substrate of Laspra.

The unfortunate consolidant action of $Ca(OH)_2$ nanoparticles held in the chapiter was the result of the petrographic and physical characteristics of Laspra dolostone, the content of soluble salts in the stone, the successive applications through the impregnation of brush strokes and the high relative humidity (85-90% RH) at which the treatment took place. These factors, increased the water content both on the surface and inside the piece, influencing the performance of the consolidant.

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ACKNOWLEDGMENTS

This work has been supported by the project HAR2011-29538 funded by the Spanish Ministry of Science and Innovation. The authors wish to thank the Archaeological Museum of Asturias for the contribution of Laspra dolostone used in this research

*Contact: arsierra@ucm.es; a.sierra@igeo.ucm-csic.es