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Evaluation of nanoparticulate consolidants applied to Novelda Stone (Spain)

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ABSTRACT: The main objective of this work is to test several nanoconsolidant treatments (pure Nano Estel, 1:1 diluted Nano Estel and Tecnadis ZR-110), with the aim of improving the intergranular cohesion of the Novelda Stone. The treatments were applied in laboratory by capillary suction and their effectiveness and depth of penetration have been evaluated on the basis of the petrophysical characteristics of the stone (petrography, elemental physical properties, hydric properties and ultrasound propagation), before and after consolidation. Subsequently, in order to estimate the durability of the treatments, accelerated ageing tests (salt crystallisation, freeze-thaw and wet-dry) were carried out. According to the results, we can conclude that none of the treatments is suitable for the treatment of Novelda stone. However, we consider that with further in-depth study Tecnadis ZR-110 could offer good results.

KEY WORDS: Durability; Cycles; Physical properties; Characterization; Novelda.

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RESUMEN: *Evaluación de consolidantes nanoparticulados aplicados a la Piedra de Novelda (España)*. El objetivo principal de este trabajo es testar varios tratamientos nanoconsolidantes (Nano Estel puro, Nano Estel diluido 1:1 y Tecnadis ZR-110), destinados a mejorar la cohesión intergranular de la Piedra de Novelda. Los tratamientos han sido aplicados en el laboratorio por succión capilar, y su eficacia y profundidad de penetración han sido evaluadas a partir de las características petrofísicas de Novelda (petrografía, propiedades físicas elementales, hídricas y ultrasonidos), antes y después de la consolidación. Posteriormente, para estimar la durabilidad de los tratamientos se han realizado ensayos de envejecimiento acelerado (cristalización de sales, hielo-deshielo y humedad-sequedad). Tras el estudio realizado se puede concluir que ninguno de los tratamientos es adecuado para el tratamiento de Novelda. Sin embargo, se considera que con un mayor estudio en profundidad el Tecnadis ZR-110 podría ofrecer buenos resultados.

PALABRAS CLAVE: Durabilidad; Ciclos; Propiedades físicas; Caracterización; Novelda.

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1. INTRODUCTION

The Novelda stone is a biocalcarenite from the eastern area of the "*comarca"* of Medio Vinalopó in Alicante (Spain) (1). It has been used as one of the main building stone in eastern Spain (1-3) and, owing to the industrial development of the nineteenth century, its use extended to the whole national territory. The geological unit from which this stone is exploited has lateral and vertical facies changes. Although the different varieties are similar in appearance, they have different petrophysical characteristics (1).

Novelda stone is very susceptible to deterioration mainly due to three factors: its carbonate nature, its clay content and the configuration of its porous system.

Its carbonate nature favours its deterioration against water due to its greater solubility, while its detrital part, with the presence of clays as a binding phase of the mineral grains, has a negative influence on its resistance to dissolution, hydration or swelling processes (4).

Another petrographic factor that influences the deterioration of this stone is its porosity. The configuration, abundance and distribution of voids determine their water behaviour and thus the entry and mobility of alteration agents inside them (5). This way, porous rocks such as Novelda are more susceptible to alteration by soluble salts than less porous, crystalline rocks

Accelerated weathering tests show that porous carbonate rocks are very sensitive to salt crystallization and have more resistant to freeze-thawing and wet-drying processes. (6-8). This has been seen for Novelda stone (1, 9)

Among the most common deterioration types affecting this stone are granular disintegration, alveolization, scaling and cracking (10-11). The degradation of Novelda stone usually occurs abruptly, by opening of a network of fissures from stone that appears to be intact on the surface. At that moment, the surface is already disaggregated, but the speed of the process prevents this phenomenon from being apparent (9).

To palliate or stop the intense deterioration that affects this stone in historical buildings, consolidating treatments are needed to improve intergranular cohesion. Both organic and inorganic consolidating agents have been employed for conservation of historical monuments (12-16). Regarding organic products these can be effective in the short and medium term. The main problem is their durability over time (13) since their nature is different from the mineral substrate, their properties are different and their behaviour over time is also different. The need for periodic reapplication of this type of product is well known in order to achieve long-term effectiveness and durability.

Therefore, it seems reasonable to use products that are more suitable and compatible with the natural stone such as inorganic products. Inorganic-based consolidants seem to have some advantages such as good durability and a physical-chemical high compatibility with the stone components, but they usually give insufficient penetration with a consequent poor strengthening effect (16).

The application of nanotechnologies allowed the development of new products for the consolidation of the stone materials obtaining more compatible long-term stable products (17). Nanoconsolidants are products with a consolidating effect based on the colloidal dispersion of inorganic nanoparticles, where the penetration of the product is greater due to the smaller size of particles (18-19). The most common nanoconsolidants are either lime or silica based. Lime based products are produced by the adding colloidal nanoparticles of calcium hydroxide to alcoholic solutions with different concentrations, so that they favour a higher carbonation speed (20-22). Silica based products are formulated with a colloidal dispersion of nanosilica in aqueous solution (22-24). After evaporation of the water, silica nanoparticles are added forming a silica matrix. Today, there are also other, less common nanoconsolidants, such as strontium hydroxide (25-26) or zirconium oxide nanoparticle dispersions.

As these new products have only recently been introduced to the market, their use requires a preliminary evaluation, by means of laboratory tests, to guarantee their suitability for the Novelda stone. The aim of this work is to test different nanoparticulated treatments applied to counteract the loss of intergranular cohesion that so frequently affects the Novelda stone.

2. MATERIALS AND METHODOLOGY

In this work, we used Novelda stone obtained from a modillion on the facade of the building of the Bank of Spain in Malaga. The entire modillion was detached from the facade due to extensive scaling processes in the rock. The cores were obtained with a Hilti tester as shown in Figure 1. The upper part of the cores were exposed to the scaling, while the rest of the stone showed no signs of alteration, this deteriorated part was not used in the study. Three cores of approximately 11 cm in diameter and lengths between 24-2 cm were used to prepare 12 slabs of 5x5x1 cm (A - L), 4 prisms of 5x5x10 cm (NV1 - NV4), 4 prisms of 5x5x9.5 cm (NV5-NV8) and 4 tablets of 2x2x1 cm (NV, NP, ND and TZ). The 5x5x1 cm slabs have been cut with the dimensions established for the vapour permeability test, while the 5x5x10 and 5x5x9.5 cm prisms have been used for the rest of the water related properties. According to the UNE-EN and CNR-ICR standards, the dimensions of the specimens for water related properties should be 5x5x5 cm, however, due to material limitations, one of the dimensions has been modified, giving priority to the length of the specimens in order to record the penetration of the treatments inside the stone.

For the cutting of the samples a diamond saw blade was used. The prisms were obtained using the centre of the cores as shown in the Figure 2, and the slabs and tablets were obtained from the remain material.

The work was planned in three phases: petrophysical characterization, intergranular stone consolidation and durability evaluation, as shown in Table 1.

2.1. Petrophysical characterization

The petrophysical characterization was based on the determination of different parameters of interest such as colour, ultrasound propagation velocity, porometric parameters, water related properties, insoluble residue, and petrographic and morphochemical analysis.

Petrographic and morphochemical analysis was carried out with the aid of an *OLYMPUS SZX16* stereomicroscope, an *OLYMPUS BX51* optical microscope, and a *Hitachi TM3000* scanning electron microscope.

The insoluble residue of the Novelda stone was obtained by acid attack with hydrochloric acid.

Quantitative colour measurement (UNE-EN 15886:2011) (13) was performed with a Chroma Meter CR-200 spectrocolorimeter on the samples referenced A to L. The illuminator was the standard C with a viewing angle of 10° and the parameters recorded were hue, saturation and luminosity. The colorimetric measurements obtained are expressed according to the nomenclature of the CIEL*a*b* and CIEL*C*h* colour spaces.

By representing the cumulative luminosity (L) curve, it was estimated that a total of 35 measure-

FIGURE 1. Location of the detached modillion and testification of the cores.

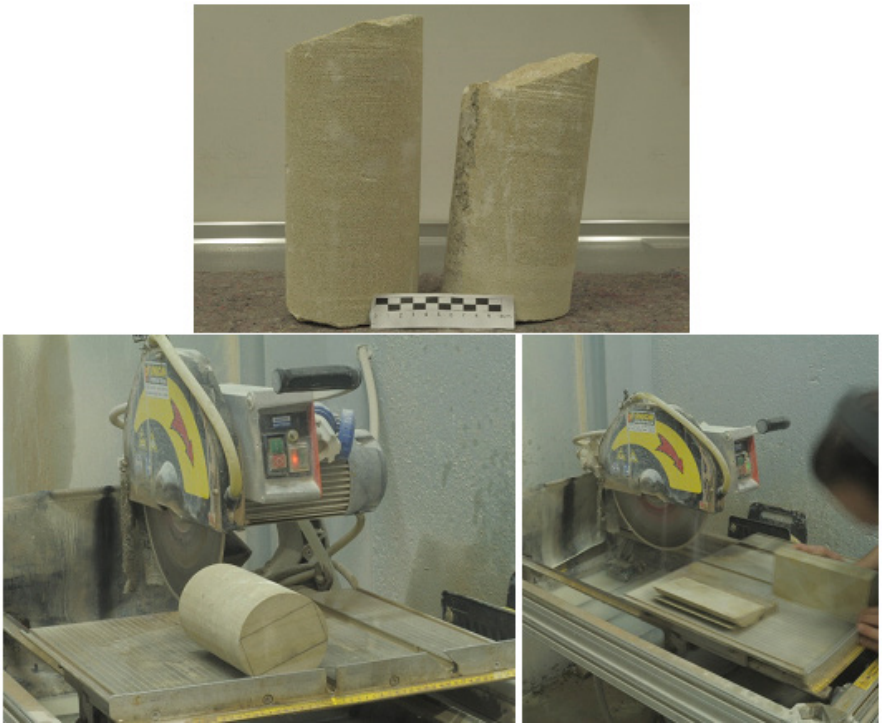

FIGURE 2. Novelda stone cores used to obtain the samples. It is shown the cut and orientation of the samples with respect to the cores.

ments for each sample would be representative of the colour. The colour changes produced by the consolidants ΔE* [1] together with their corresponding values in a standardized grey scale GSc (UNE-EN ISO 105-A05: 1998) (21) were calculated according to Equation [1]:

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \qquad [1]$$

where:
L*: luminosity
a* y b*: chromatic coordinates measuring red-green and blue-yellow directions

To obtain the velocity of P wave propagation (UNE-EN 14579:2005) (14), a Pundit Plus ultrasonic equipment was used following the transparency method, on samples NV1-NV8. The frequency of the transducers used is 1 MHz, with a contact surface of 176.72 mm^2. For better transmission, honey was used as couplant.

Mercury injection porosimetry (ASTM D4404-84:1998) (15) was performed with a Micromeritics Auto Pore porosimeter on sample NV. Finally, the following water related properties were determined on samples A-L and NV1-NV8:

(i) forced vacuum absorption according to the UNE-EN 1936:2007 standard (16), (ii) water desorption according to the UNE-EN 16322:2013 standard (17), (iii) free water absorption following the UNE-EN 13755:2008 standard (18) (iv) water absorption by capillary suction under the UNE-EN 15801:2010 standard (19) and (v) water vapor permeability according to the UNE-EN 15803:2010 standard (20).

2.2. Consolidation

The intergranular consolidation of Novelda stone was carried out using two products: Nano Estel and Tecnadis ZR-110. Nano Estel is an aqueous colloidal silica dispersion of nanometric dimensions (10-20 nm), and Tecnadis ZR-110 is an aqueous zirconium oxide dispersion and nanoparticulated powder (10-15 nm).

Nano Estel was applied both in pure state and diluted with 1 part of demineralized water, thus carrying an active matter percentage of 15%. Tecnadis ZR-110 was applied in pure state only. In all cases, the product was applied by capillary suction at a constant temperature of 20ºC.

After the application of the treatment, the samples were left to dry in a fume hood for three weeks. Afterwards, they were placed in the oven at 60ºC for a minimum of 48 hours until they reached their constant weight

Due to material limitations, two prisms and three slabs were consolidated with each treatment, plus one tablet per treatment to assess mercury injection porosimetry (Table 1).

To evaluate the consolidation of the samples, the petrophysical characterization was repeated following the above-described procedures: colorimetry, ultrasonic measurement, porometry and water related properties, as shown in Table 1. In addition, a cross-section cut of one of the slabs per treatment was used in order to be studied in the SEM.

2.3. Durability

In order to evaluate the durability of the Novelda stone after its consolidation, three accelerated aging tests were carried out: salt crystallization, freeze-thaw and wet-dry tests. The number of cycles varied according to the resistance of the stone and the aggressiveness of the test.

For the salt crystallization test, cycles of 24 hours were run. Each cycle comprised two stages: immersion and drying. Anhydrous sodium sulphate (Na_2SO_4) was applied in a 14% aqueous solution. The following samples were used: NV2 (pure Nano Estel), NV4 (1:1 diluted Nano Estel), NV6 (Tecnadis ZR-110) and NV8 (blank). The cycles consisted of totally submerging the samples in saline solution at room temperature for 4 hours and then drying them in an oven at constant temperature of 105ºC for 20 hours, this way a thermal shock was also applied. The cycles were repeated until the samples broke down in the third cycle. The behaviour of the samples during the test was monitored through macroscopic observation, with photographic record and dry weighing in the second and third cycles.

The freeze-thaw test consisted of successive cycles of 24 hours. Each cycle comprised two stages: freezing and thawing. The test was performed on samples NV1 (pure Nano Estel), NV3 (1:1 diluted Nano Estel), NV5 (Tecnadis ZR-110) and NV7 (blank). Prior to the cycles, the samples were soaked in water by free immersion for two days. Then the samples were frozen at -23ºC for 20 hours under dry conditions and thawed while submerged in water at room temperature for 4 hours. A total of 20 cycles were run. The damage was monitored throughout the test by macroscopic observation with photographs, dry weighing, and ultrasonic study, every 10 cycles.

During the wet-dry test, the samples were subjected to 24-hour cycles divided into two stages: fogging and drying at room temperature. For this test, the following samples were used: A, B (pure Nano Estel), D, E (1:1 diluted Nano Estel), G, H (Tecnadis ZR-110) J and K (blanks). The cycles consisted of fogging the specimens with water, in the fog chamber, for 8 hours, and then drying them at room temperature for 16 hours. A total of 10 cycles were run. Throughout the test, controls were made every 5 cycles, recording weight variations, and studying the colour on the faces were consolidants were applied, to evaluate possible colour changes.

The prisms were used for the salt crystallization and freeze-thaw tests in order to be able to work on

Table 1. Methodology of the study and sample references. n: number of samples studied.

	PETROPHYSICAL CHARACTERIZATION	CONSOLIDATION	DURABILITY
SEM	C, F, I, L	C, F, I, L	
Colour	A-L (n:12)	A-I (n:9)	NV1-NV8 (n:8) A, B, D, E, G, H, J, K (n:8)
Ultrasound Study	NV1-NV8 (n:8)	NV1-NV6 (n:6)	NV1, NV3, NV5, NV7 (n:4)
Porometric Analysis	NV (n:1)	NP, NV, TZ (n:3)	
Water Properties Forced vacuum absorption Water desorption Free water absorption Water absorption by capillary suction Water vapor permeability	 NV1-NV8 (n:8) NV1-NV8 (n:8) NV1-NV8 (n:8) NV1-NV8 (n:8) A-L (n:12)	 NV1-NV6 (n:6) NV1-NV6 (n:6) A-I (n:9)	
Intergranular Consolidation Blanks Pure Nano Estel 1:1 diluted Nano Estel Tecnadis ZR-110		 NV7-NV8, J-L (n:5) NV1-NV2, A-C, NP (n.6) NV3-NV4, D-F. ND (n:6) NV5-NV6, G-I, TZ (n:6)	
Accelerated Aging Test Salt crystallization Freeze-thaw Wet-dry			NV2, NV4, NV6. NV8 (n=4) NV1, NV3, NV5, NV7 (n=4) A, B, D. E, G, H, J, K (n=8)

a larger surface to record the damage, while the slabs were used in the wet-dry test since it is not such an aggressive test, and the objective were to observe colour changes. Due to material limitations, only one prism and two slabs per treatment could be used in each test.

Colour changes for all tests were calculated with respect to the values of the untreated stone and compared with the changes obtained after consolidation.

3. RESULTS

3.1. Petrophysical characterization

Characteristics of the Novelda stone used in this study are summed up in Table 2.

Macroscopically, the Novelda stone is a granular and coherent rock with a beige-yellowish coloration. Some voids of 0.5 mm diameter size can be observed, but they are not very abundant.

Microscopic study showed that the stone has a clastic texture formed by abundant fossils (foraminifera, bryozoans and bivalves) (50-55%), and quartz and terrigenous phyllosilicates in smaller proportions (20-25%). Grain size ranges from 0.1 to 0.3 mm. Grains are embedded in a calcite cement of sparite (10-15%) with a minor proportion of calcareous and clay matrix (5%). Microscopically recognisable porosity is not very abundant. The observed pores have elongated to round shapes, diameter sizes between 0.02-0.3 mm and low connection.

By SEM study we obtained a calcitic composition, with minor amounts of magnesium, and rich in silicon with traces of aluminium, iron and potassium. The intergranular material, composed mainly of calcite, shows zones richer in aluminosilicates and rounded pores ranging in size from 100 to 300 μm. Calcitic cementation consists of precipitation of sparite crystals of variable sizes depending on pore size and occupying inter- and intra-bioclastic positions. In other cases, the precipitation of calcitic cement occurs in large extensions along the stone and presents microcracks with variable lengths between 50 and 130 microns and openings of 2-10 μm, possibly formed by shrinkage processes in clays.

The insoluble residue test revealed a 76% of carbonate fraction and 24% of terrigenous fraction, of which 20% belongs to the coarse fraction and 4% to the fine fraction.

Mercury injection porosimetry measurements on the Novelda stone revealed an open porosity of 18.8% with a high specific surface area of 2.6 m^2/g and an apparent density of 2,156 kg/m^3. It is a microporous rock with an average pore throat radius of 0.07 μm and a median of 0.9 μm. This porosity can be divided into two pores families: one between 10-0.1 μm (70-80% of total porosity) and another one under 0.1 μm (around 30-20%).

The Novelda stone studied in this research is quite homogeneous, no major changes were detected in the propagation velocity of the P waves along the prisms. Obtained values oscillate from one specimen to another between 3,450 and 3,615 m/s.

The forced vacuum absorption test yielded an average apparent density of 2,134 kg/m^3, and a high open porosity of 21.1% with an elevated water saturation content of 9.9%.

Absorption kinetics are fast, the water content in the first hour of the test is 5.3%, meanwhile at the end of the test it reaches a 7.5% corresponding to a degree of saturation of 85.8%. The remaining 24% indicate that there is a poorly communicated porosity, which is not easily accessible to water (Figure 3).

Desorption kinetics are slow, at the end of the test, after 7 days, saturation degree (S_{7d}) reached 7.9% with a with a retained water content of 0.8% (Figure 3). Water desorption test was carried out after saturation from forced vacuum absorption test.

Capillary kinetics are slow with a low capillary absorption coefficient of 2 kg/m^2 x h$^{1/2,}$ probably related to the highly tortuous system. The capillary penetration coefficient is 1.4 cm/h$^{1/2}$.

The Novelda stone has a high water vapor permeability coefficient of 203 g/m^2 x 24h.

3.2. Consolidation assessment

3.2.1. Colour

As shown in Table 3, the higher the GSc value, the slighter the colour changes. The colour change produced by the pure Nano Estel is hardly visible to the human eye, while the diluted product (1:1) caused significant changes. Regarding Tecnadis ZR-110, the colour changes were very slight, but micro cracking was induced by the treatment.

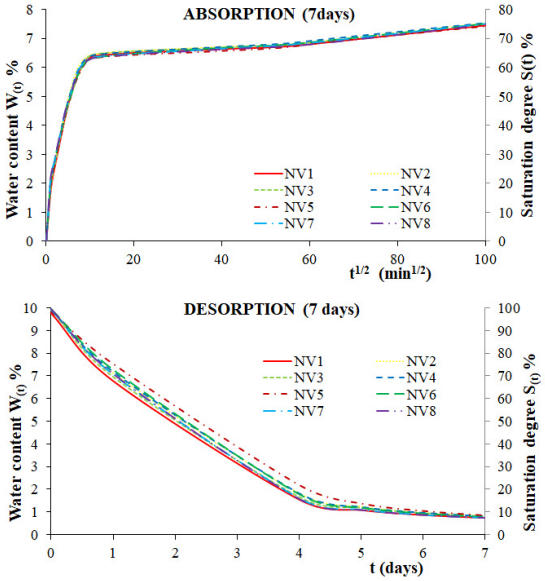

FIGURE 3. Absorption and desorption kinetics for the Novelda stone (blank).

TABLE 3. Colour changes after consolidation treatment.

CONSOLIDANT	ΔE*	GSc	CHANGES TO HUMAN EYE
Pure NANO ESTEL	0.99	4.5	Hardly visible
1:1 diluted NANO ESTEL	7.66	2	Significant
TECNADIS ZR-110	1.96	4	Very slight

TABLE 2. Characteristics petrophysical of Novelda stone.

NOVELDA STONE (BLANK) PETROPHYSICAL CHARACTERIZATION				
Petrography	Beige-yellowish biocalcarenite		Grains: bioclasts (50-55%); terrigenous (20-25%) Union phase: cement (10-15%); matrix (5%)	
Colour	L*: 75 ± 1	a*: 0.9 ± 0.1	b*: 15 ± 0.4	c*: 15 ± 0.4
Ultrasound Study	Homogeneous; Vp: 3518 ± 34 m/s			
Forced vacuum absorption	Apparent density (ρ_d): 2134 ± 3 kg/m^3 Open porosity (n_0): 21.1 ± 0,1 %		Saturation water content (Ws): 9.9 ± 0.1 %	
Water desorption	Water content W_t (%)	1 hour: 9.7 ± 0.05	2 days: 5.3 ± 0.2	7 days: 0.8 ± 0.03
	Saturation degree S_t (%)	1 hour: 98.1 ± 0.4	2 days: 52 ± 2	7 days: 7.9 ± 0.4
Free water absorption	Water content W_t (%)	1 hour: 5.3 ± 0.1	2 days: 6.75 ± 0.05	7 days: 7.5 ± 0.04
	Saturation degree S_t (%)	1 hour: 60 ± 1	2 days: 68.3 ± 0.5	7 days: 75.8 ± 0.4
Water absorption by capillary suction	Capillary absorption coefficient C: 2 ± 0.4 kg/m² x h$^{1/2}$ Capillary penetration coefficient A: 1.4 ± 0.2 cm/h$^{1/2}$			
Water vapor permeability	Water vapor permeability coefficient Kv : 203 ± 13 g/m^2 x 24h			
Porometric Analysis	Apparent density: 2156 kg/m^3		Corrected density: 2626 kg/m^3	Open porosity: 18.8%
	Pore throat radius:	Average: 0.07 µm		Surface area: 2.6 m^2/g
		Median: 0.88 µm		

3.2.2. Porometric study

The changes in the open porosity of the treated rock are slight, so that the specimens consolidated with pure Nano Estel and 1:1 diluted Nano Estel decrease their porosity by about 1%, while with Tecnadis ZR-110 it increases by 1%. On the other hand, the specific surface area increases for Nano Estel diluted 1:1 and Tecnadis ZR-110, being more noticeable with the first treatment, while pure Nano Estel causes a decrease in the specific surface area of the specimens (Table 4).

After the consolidation treatments, the distribution of macroporosity varies slightly, with only a noticeable decrease in the number of pores with pore throat radii between 7.5 and 10 µm, but none of the pore throat radii greater than 10 µm were filled.

The configuration of microporosity was significantly modified (Figure 4), a decrease in the pores with pore throat radii between 4-7.5 µm was observed. New pore throat radii were generated around 3 µm, consolidants seem to be particularly effective in this radius range, especially Tecnadis ZR-110.

An increase in the number of pores with pore throat radii around 1 µm and below 0.001 µm, and a decrease in the radius range around 0.1 µm was observed. This effect is the most evident in the case of the 1:1 diluted Nano Estel.

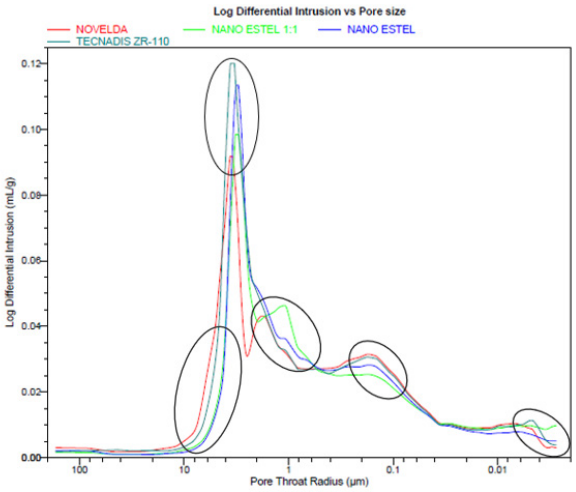

FIGURE 4. Mercury intrusion curves for unconsolidated Novelda stone-blank (red), consolidated with pure Nano Estel (blue), 1:1 diluted Nano Estel (green) and Tecnadis ZR-110 (bluish grey).

3.2.3. SEM+EDX

Since the treatments affect the microporosity of the Novelda Stone it has been difficult to locate them inside the specimens, however, as the ultrasound results showed, for the 1:1 diluted Nano Estel and Tecnadis ZR-110 we found a higher concentration of the products at the base of the samples, which was easily recognisable by SEM.

The study of the larger pores near the 1:1 diluted Nano Estel application surface shows the presence of the consolidant filling and covering the pores (Figure 5). The treatment appears with a glassy texture similar to the conchoidal fracture of the obsidian.

TABLE 4. Porometric parameters after consolidation treatment.

OPEN POROSITY (%)			
NOVELDA STONE (BLANK)	**PURE NANO ESTEL**	**1:1 DILUTED NANO ESTEL**	**TECNADIS ZR-110**
18.8	18.2	18.0	20.0
SPECIFIC SURFACE (m2/g)			
NOVELDA STONE (BLANK)	**PURE NANO ESTEL**	**1:1 DILUTED NANO ESTEL**	**TECNADIS ZR-110**
2.62	2.46	3.18	2.88

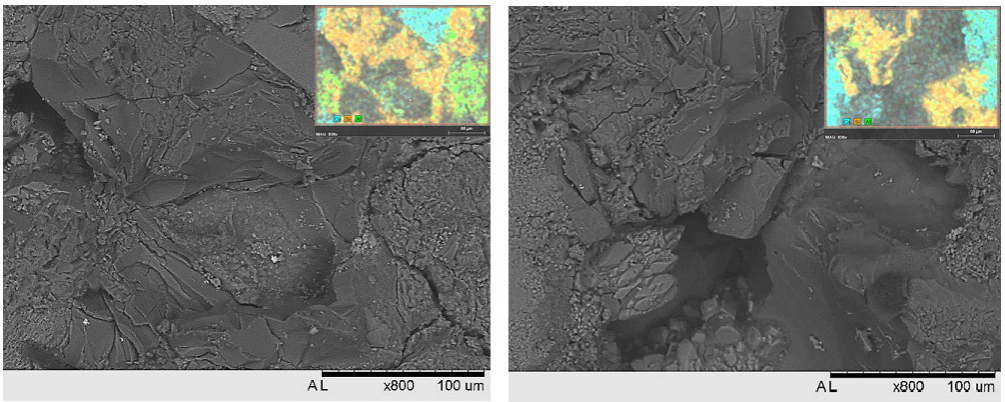

FIGURE 5. Detailed micrographs of pores filled with 1:1 diluted Nano Estel in slab F. Elemental mapping with calcite (blue), silica (orange) and aluminium (green) is shown. Aluminium is shown in order to distinguish the consolidant from the phyllosilicates.

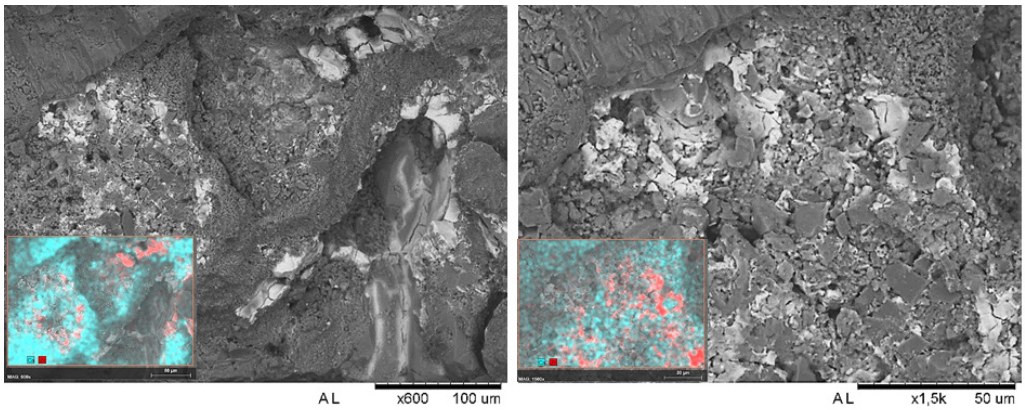

FIGURE 6. Detailed micrographs of the longitudinal section of slab I consolidated with Tecnadis ZR-110. Elemental mappings with zircon (red) and calcite (blue) are shown.

Tecnadis ZR-110 appears at the base of the sample creating a film on the cement and pores. It is not a continuous film but appears cracked and discontinuously distributed (Figure 6). This cracking contributes to an increase in microporosity as the treatment itself is creating new pores.

3.2.4. Ultrasound propagation

The efficiency of consolidating treatments is the highest in the first 1.5-3 cm from the base of the samples. This is revealed by an increase in P-wave velocity in that zone. The measured increase was around 1.5% for pure Nano Estel, 2.9% for 1:1 diluted Nano Estel and 2.7% for Tecnadis ZR-110, taking into account that these percentages correspond to the average of the measures taking in the first 3 cm. Distribution of treatments is shown in Figure 7.

The pure Nano Estel is distributed homogeneously along the first 1.5-3 cm. The penetration depths of 1:1 diluted Nano Estel are similar to those of the pure product, but the concentration is higher in the first 1.5 cm. The concentration of Tecnadis ZR-110 is also higher in the first 1.5 cm. This is manifested by a steep increase in P wave velocity in this lower part of the samples. In consolidated areas the treatments produce an improvement in cohesion (increase in V_P) compared to unconsolidated values.

As was seen in the porosity study, the Tecnadis ZR-110 provided a slight increase in porosity which was not reflected in the ultrasound study. This was explained by the fact that the treatment produced a new microporosity, so at the same time is filling larger pores but creating new smaller ones. However, this only occurred in the first 1.5 cm of the base of the sample, which causes the observed increase in P wave velocity. The rest of the specimen was not affected by the treatment and therefore no changes in the ultrasound profile appeared.

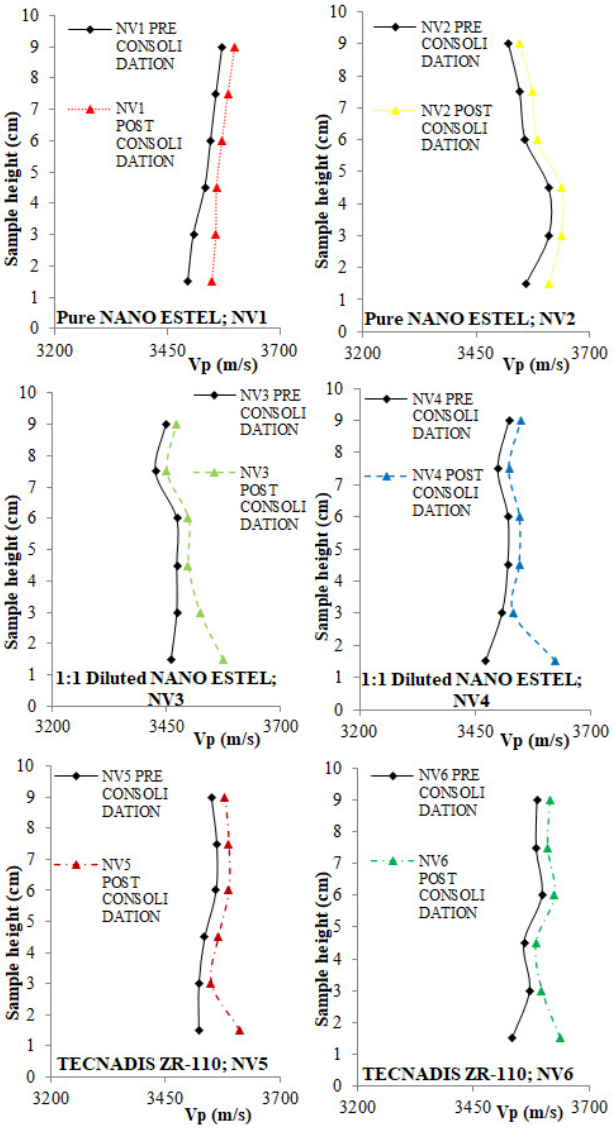

FIGURE 7. Elastic wave propagation profiles before and after consolidation of Novelda stone.

TABLE 5. Forced vacuum absorption results after treatment.

	NANO ESTEL	1:1 DILUTED NANO ESTEL	TECNADIS ZR-110
Apparent density (ρ_d; kg/m^3)	2135.4 ± 3.2	2135.7 ± 0.9	2133.1 ± 0.3
Open porosity (n_0; %)	20.93 ± 0.11	20.92 ± 0.02	21.10 ± 0.04
Saturation water content (Ws; %)	9.80 ± 0.07	9.79 ± 0.01	9.90 ± 0.02

3.2.5. Water related properties

Water content in saturation (Ws), density of dry rock (ρ_d) and open porosity (n_0) suffer slightly changes after the treatments. Due to the filling of the pores, the porosity decreases. The average values for the treated rock samples are given in Table 5.

Desorption kinetics were affected by the new microporosity generated by the nanoconsolidants. In the treated samples, desorption is slower and the content of water in retention is higher (Figure 8). Saturation degree at seven days (S_{7d}) was 7.9% in the unconsolidated samples, and it reached 13% in the treated ones. In general, the behaviour of all treated samples is similar to each other, and it differs from their pre-treatment behaviour. However, the sample treated with 1:1 diluted Nano Estel is slightly different to the other samples due to the more noticeable change in porosity (Figure 8).

Water vapour permeability (K_V) shows a slight increase with respect to the untreated stone and ranges between 206 and 215 ± 15 g/m^{2}x24h, with no apparent differences between treatments. This is because water in vapor form moves through larger pores, which were not affected by consolidation.

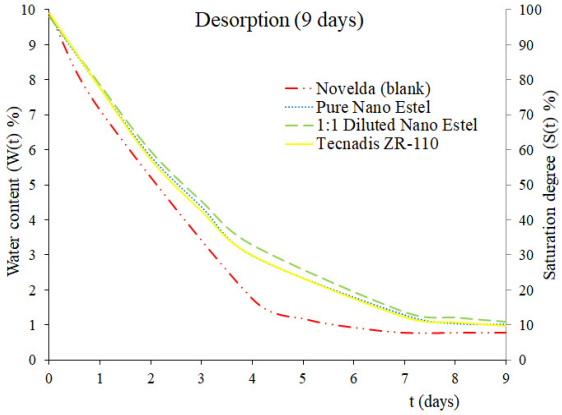

FIGURE 8. Desorption kinetics for the Novelda stone (blank) before and after the treatments.

3.3. Durability evaluation

3.3.1. Salt crystallization

Salt crystallization test resulted in a significant loss of material from the first cycle. The samples broke

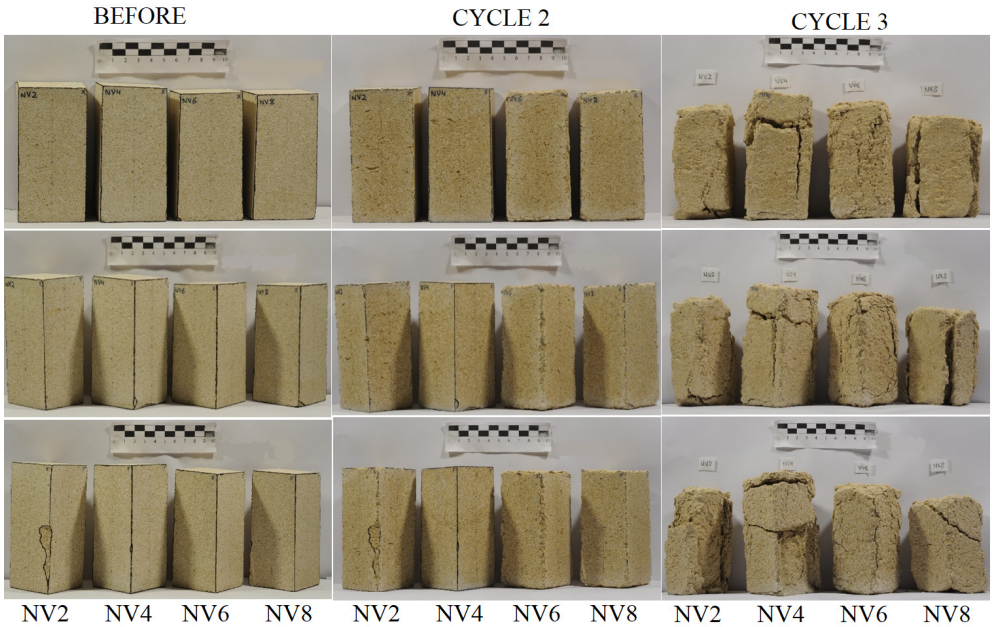

FIGURE 9.Front and lateral views of samples before and during salt crystallization test. NV2: Pure Nano Estel; NV4: 1:1 diluted Nano Estel; NV6: Tecnadis ZR-110; NV8: Blank.

down in the third cycle, after which the test was not continued. The material loss made it impossible to carry out ultrasound measurements to assess the damage after the test.

The sample consolidated with pure Nano Estel suffered the highest weight loss (31%), followed by the blank with 19%. Weight loss of the sample treated with 1:1 diluted Nano Estel was 7%, and the sample treated with Tecnadis ZR-110 lost 6% of its weight. Figure 9 demonstrates the observed surface damage.

Due to the crystallization of salt both in the surface and inside the prisms, four samples suffer granular disintegration causing large material losses. These losses occurred more homogeneously throughout the untreated sample, while the consolidated prims suffered more disintegration in the upper parts where the treatments were not effective.

The following is a more detailed description of the damage observed for each sample at the end of the test:

NV2 sample; pure Nano Estel. This sample suffered loss of material on all its faces, losing some fragments of 0.5 cm length and 0.1 cm width. The deterioration occurred in the form of spalling, so that entire slabs of material were detached leaving the interior of the stone uncovered in some sections. Also hairline cracks appeared with apertures of 0.1-0.5 cm.

NV4 sample; 1:1 diluted Nano Estel. The base of the sample resisted better and only suffered spalling in one of its faces losing a fragment of 0.5 cm, while in the upper part hairline cracks appeared with apertures between 0.1-0.8 cm. These fractures spread through the faces causing this complete section to separate from the rest of sample and divided it into two pieces.

NV6 sample; Tecnadis ZR-110. This is the sample that best preserved its initial structure, it did not suffer any spalling, but we found hairline cracks with apertures around 0.1 cm, especially in the upper part of the sample.

NV8 sample; blank. Significant loss of material was observed on this sample, resulting in a 1.5 cm decrease in length. Hairline cracks appeared that cross several faces with apertures between 0.1-0.6 cm and form slabs of material parallel to the long axis of the prism.

All samples suffered extreme colour changes (Table 6) due to the crystallization of the salts, which generated whitish colorations. Colour changes were measured on the prisms without washing the salt.

3.3.2. Freeze-thaw

The freeze-thaw test was run for 20 cycles. It caused very slight weight losses, around 0.3%, and superficial pitting, in all the prisms, due to either loss of clays or loss of grains and cement in specific areas.

The ultrasound study revealed the internal damage suffered by the samples due to the action of ice (Figure 10).

In general, the untreated and treated samples behaved similarly, showing the same decreasing trend in terms of post-cycle values. Both the blank and the sample treated with 1:1 diluted Nano Estel showed a 2.4% decrease in the velocity of P wave propagation. In the sample treated with pure Nano Estel the decrease was 1.9%; while for the sample treated with Tecnadis ZR-110 the value was 1.5% lower. In this way, the percentage change in the sample treated with 1:1 diluted Nano Estel is higher than for the other treatments, as shown in Figure 10.

It should be noted that in the samples consolidated with 1:1 diluted Nano Estel and Tecnadis ZR-110 the damage suffered at the base is less significant than in

Table 6. Colour changes after salt crystallization test.

	CONSOLIDATION			SALT CRYSTALLIZATION		
Consolidant	**ΔE***	**GSc**	**Changes to human eye**	**ΔE***	**GSc**	**Changes to human eye**
BLANK	-	-	-	46	1	Extreme
Pure NANO ESTEL	0.99	4.5	Hardly visible	42	1	Extreme
1:1 diluted NANO ESTEL	7.66	2	Significant	34	1	Extreme
TECNADIS ZR-110	1.96	4	Very slight	62	1	Extreme

Table 7. Colour changes after freeze-thaw test.

	CONSOLIDATION			FREEZE- THAW		
Consolidant	**ΔE***	**GSc**	**Changes to human eye**	**ΔE***	**GSc**	**Changes to human eye**
BLANK	-	-	-	22	1	Extreme
Pure NANO ESTEL	0.99	4.5	Hardly visible	8	1.5	Very significant
1:1 diluted NANO ESTEL	7.66	2	Significant	28	1	Extreme
TECNADIS ZR-110	1.96	4	Very slight	21	1	Extreme

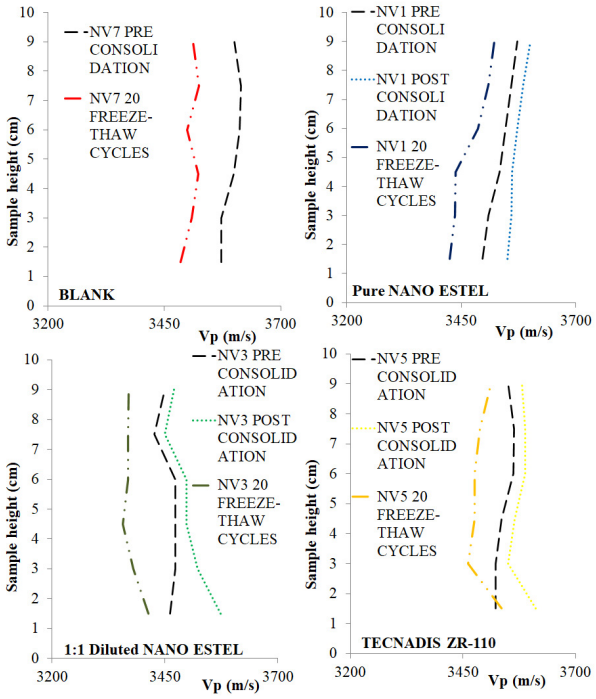

FIGURE 10. Elastic wave propagation profiles during the freeze-thaw test.

the rest of the samples due to the higher effectiveness of the consolidant in these areas.

After the test, we observed extreme colour changes in the blank and in the samples consolidated with 1:1 diluted Nano Estel and Tecnadis ZR-110. For the pure Nano Estel the change was very significant (Table 7).

3.3.3. Wet-dry

10 cycles of the wet-dry test were performed with weight losses around 0.1%.

Significant changes in colour were registered after the test (Table 8), samples treated with pure Nano Estel and 1:1 diluted Nano Estel showed an observable colour change after the test, however after treatment the change was hardly visible for the first treatment and significant for the second. This way, colour change after wet-dry test was higher for the sample treated with pure Nano Estel.

On the other side, slab treated with Tecnadis ZR-110 showed a very slight colour change after test.

For the sample as blank colour differences are hardly perceptible for the human eye.

4. DISCUSSION

The porous system of the Novelda stone could be divided into a macroporous (≥ 7.5 µm) and a microporous (< 7.5 µm) fraction. The water vapour permeability coefficient (203 g/m² x 24h) indicated good connectivity of the macroporous fraction. After the treatments, water vapour permeability maintained or slightly increased compared to untreated stone, this is because water vapour moves through the pores larger than 7.5 µm, which were not much affected by consolidation.

On the other hand, desorption was slow with a high water retention content (0.8%), which can be related both to the high percentage of micropores and the high specific surface area (2.6 m²/g), and to the presence of clays capable of retaining water. Even though Novelda stone has high microporous fraction, the kinetics of capillary absorption was slow with a low capillary coefficient (2 kg/m² x $h^{1/2}$), which had been related to a very tortuous system.

Since the type of Novelda stone analysed in this study was unknown, it was difficult to establish with certainty the variety. However, the results were consistent with those studied by Fort et al. (2002) (1) on the different varieties of Novelda stone, showing physical properties very similar to those determined for the Bateig Llano variety.

Regarding the consolidation with nanoparticulated treatments, all the tested consolidants (pure Nano Estel, 1:1 diluted Nano Estel and Tecnadis ZR-110) penetrated the stone effectively in the first centimetres of the base of the samples, corresponding to the area of application of the treatment. With pure and 1:1 diluted Nano Estel, the consolidating effect was registered up to 1.5-3 cm, while Tecnadis ZR-110 reached penetration depths of around 1.5 cm. However, due to the lower viscosity of the 1:1 diluted Nano Estel and Tecnadis ZR-110, there is a higher concentration of these products at the base. Penetration depths obtained are high compared to other studies with nanoconsolidants (12, 13).

Petrophysical changes took place after all treatments. There was an alteration of the microporosity,

TABLE 8. Colour changes after wet-dry test.

	CONSOLIDATION			WET-DRY		
Consolidant	**ΔE***	**GSc**	**Changes to human eye**	**ΔE***	**GSc**	**Changes to human eye**
BLANK	-	-	-	0.4	4.5	Hardly visible
Pure NANO ESTEL	0.99	4.5	Hardly visible	3.1	3	Observable
1:1 diluted NANO ESTEL	7.66	2	Significant	2.6	3	Observable
TECNADIS ZR-110	1.96	4	Very slight	1.5	4	Very slight

and a slight decrease of the macroporosity, which resulted in slower evaporation kinetics, with higher water retention. However, the distribution of consolidants was not equal in all cases. For the samples treated with pure Nano Estel, more homogeneous distribution was obtained, while the 1:1 diluted Nano Estel and Tecnadis ZR-110 concentrated in the base of the samples.

The salt crystallization test revealed that Novelda stone is highly susceptible to the action of soluble salts. The serious damages induced in the samples are mainly due to the increase in volume that takes place when the salts crystallize or pass from anhydrous to hydrated states inside the pores. Pure Nano Estel proved to be the least effective treatment against salt crystallization. The sample treated with this product suffered more serious surface damage than the untreated sample. The 1:1 diluted Nano Estel protected the base of the sample from further damage, but the upper part, where the treatment was not effective, was severely affected due to the differential behaviour between consolidated and unconsolidated surfaces. Tecnadis ZR-110 shows the best results, as it significantly reduced the damage produced by salts.

The stone was found to have high resistance against the action of ice, and the damages suffered both superficially and internally were minor. The deterioration attributed to the cyclic action of ice is due to the increase of volume inside the porous system, during the change from liquid to solid phase. In general, all the specimens showed a behaviour similar to the blank. The sample treated with Tecnadis ZR-110 yielded the best results, especially at the base of the sample, where the product was present in higher concentration. After the test, we observed a decrease in the luminosity of Novelda stone, with extreme colour changes in the blank and in the samples consolidated with 1:1 diluted Nano Estel and Tecnadis ZR-110. For the pure Nano Estel the colour change was very significant.

The wet-dry test did not produce any physical damage in the specimens, other than loss of clays, however, significant changes in colour were registered. In the stone treated with the pure Nano Estel, the water seems to react with the product in such a way that there is an observable chromatic change, with respect to the untreated stone. Regarding the 1:1 diluted Nano Estel an observable colour change was also registered, however this change is less than the one obtained with the pure treatment. On the other side, slab treated with Tecnadis ZR-110 showed a very slight colour change after test.

5. CONCLUSIONS

The performed durability study indicates that Novelda stone has high resistance to the aggressive action of water, both in solid and in liquid state. Nevertheless, the stone is highly susceptible to deterioration in the presence of soluble salts.

Among the tested treatments, pure Nano Estel yielded the worst results in terms of recovering intergranular cohesion. As a result of salt crystallization, the sample treated with this product suffered an even greater loss of material than the untreated stone. It also showed evident colour changes, when submitted to the action of water in the wet-dry test.

1:1 diluted Nano Estel improved the cohesion in the base of the sample where the product acted, but in the upper part the damage was more severe; it even detached from the base, in the salt crystallization test. The freeze-thaw test had a similar effect on the samples treated with this product as the salt crystallization test, although the base suffered even less damage. This treatment also caused evident colour changes due to the action of water in the wet-dry test.

Tecnadis ZR-110 is the consolidant that offers the best results. An improvement of the intergranular cohesion was observed in the salt crystallization test, although the samples still suffered serious damage. An improvement was also observed in the behaviour against the action of ice, especially at the base of the samples, with a very slight colour change in the wet-dry test.

After this research, none of the treatments used can be recommended as they all show poor performance in the salt crystallisation test.

However, we believe that Tecnadis ZR-110 could be a product to be taken into account. It would be necessary further investigation where the freeze-thaw and wet-dry tests could be carried out for a longer period of time, and to adjust the conditions of the salt crystallisation test to make it less aggressive and thus be able to obtain more data.

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