Environmental Earth Sciences (2018) 77:302
https://doi.org/10.1007/s12665-018-7491-6

THEMATIC ISSUE

Assessment of the efficacy of ethyl silicate and dibasic ammonium phosphate consolidants in improving the durability of two building sandstones from Andalusia (Spain)

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Received: 15 November 2017 / Accepted: 10 April 2018 / Published online: 16 April 2018

Abstract

We performed a comparative study of the effectiveness of ethyl silicate (TEOS) and dibasic ammonium phosphate (DAP) on two varieties of natural stone used in the architectural heritage of Andalusia (Spain): Arenisca Ronda (calcarenite) and Molinaza Roja (arkose). The consolidants were applied on healthy samples with a paintbrush, a method frequently used in real building works, and the study was divided into three phases: (a) petrophysical analysis and analysis of the porous system prior to application of the consolidants; (b) evaluation of the changes that have taken place after each application; (c) evaluation of the durability of the two varieties of treated rock when subjected to the salt crystallization ageing test. The results obtained show that there is a compositional affinity between the consolidant and the rock and that this affinity has an influence on the efficacy of the product. This explains why DAP performed better in Arenisca Ronda, which is rich in carbonates, while TEOS was more effective for Molinaza Roja, which is rich in silicates. The change in the porous system was not important, although it showed positive aspects such as an improvement in the drainage of the water during the drying process. We also measured the level of penetration of both products, which reached a depth of 3–5 mm depending on the product applied. We also noticed a negative result, namely the change in the colour of both rocks after treatment with the consolidants, especially in the case of DAP. Finally, the stones were subjected to a salt crystallization test, the results of which show that the consolidants increased the durability of the materials.

Keywords Carbonated sandstone · Siliceous sandstone · Dibasic ammonium phosphate (DAP) · Ethyl silicate (TEOS) · Consolidation

Introduction

Over the last century, our architectural heritage has suffered considerable damage and this has led to increasing awareness of the need for its conservation and restoration (Gómez-Heras and McCabe 2015). Since the 1960s, the development of products that slow down and/or minimize the deterioration of building and ornamental materials has increased dramatically (Doehn and Price 2010). Nonetheless, and in general terms the study of consolidation treatments has focused above all on analysing the products, the concentration and the solvent in which they should be diluted (Doehn and Price 2010), leaving an important gap as regards the methodology of application or the contact time necessary between the product and the material in order for the consolidation process to be completely effective (Ferreira Pinto and Delgado Rodrigues 2012). In the restoration of our ancient buildings, the current trend is

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This article is part of a Topical Collection in Environmental Earth Sciences on "Stone in the Architectural Heritage: from quarry to monuments – environment, exploitation, properties and durability", guest edited by Siegfried Siegesmund, Luís Sousa, and Rubén Alfonso López-Doncel.

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for prevention rather than substitution and/or replacement of the damaged material (Fort 2006; Matteini 2008). In order for this prevention to be as effective as possible, great efforts have been made in recent years to provide an exact definition of the concept of "consolidation", so as to be able to establish a standard criterion that would enable researchers to compare the efficacy of the products currently on the market for consolidating different types of rock in a standardized manner. Ferreira Pinto and Delgado Rodrigues (2012) proposed the creation of a standard protocol to regulate the effectiveness of the consolidation treatments, in which they identify two separate phases: the objective of the first phase is to evaluate the potential capacity of a particular type of rock to absorb and retain the consolidant product inside it, while in the second phase, the aim is to select the most suitable treatment procedure for each kind of rock so that the consolidant effect, in terms of an increase in the mechanical resistance and cohesion of the material, is as good as possible in both laboratory tests and real situations.

For these reasons, research is now focusing not only on the study of the type of consolidant and its proportions, but also on the best possible application method (Ferreira Pinto and Delgado Rodrigues 2008; Franzoni et al. 2015a, b) or the degree of compatibility between the product and the substrate (Rodrigues and Grossi 2007; Ferreira Pinto and Delgado Rodrigues 2012) so as to ensure better product-rock cohesion. It is also essential to bear in mind that the choice of the method of application will always depend on the particular piece that needs to be treated (type of material, dimensions, whether or not it is painted, degree of decay, etc.) and on where this has to be done, in the laboratory or "in situ" and in any case, before making this choice, it is necessary to study the environmental conditions to which the building is exposed (Snethlage and Sterflinger 2011).

The efficacy of the consolidant depends on various factors, the most important of which are the compatibility between the consolidant product and the material being treated, and the degree to which the product penetrates inside the material (Ferreira Pinto and Delgado Rodrigues 2008; Borsoi et al. 2016). The compatibility will depend on the chemical composition of the damaged material and the consolidant, while the degree of penetration depends on the porous system (Wheeler 2005). Researchers have also found that the same material can behave differently towards external decay factors depending on its specific intrinsic properties (Colella et al. 2017; De Cock et al. 2017). It is therefore essential to consider any cultural asset as a unique object and subject it to an exhaustive preliminary study to find out more about its particular characteristic properties, the pathologies affecting it and its current state of decay. With this information, the conservator or restorer can select, together with other professionals from different scientific fields, the most effective product and the best method for applying it so as to ensure the success of the treatment.

As regards the different methods used to consolidate stones, new products are continually being developed (Matteini et al. 2011; Sassoni et al. 2011; Zhang et al. 2013; Ludovico-Marques and Chastre 2014; De Rosario et al. 2015; Franzoni et al. 2015a, b; Naidu et al. 2015; Zornoza-Indart and Lopez-Arce 2017). Until recently, the products with a siliceous composition, such as tetraethyl orthosilicate (commonly known as ethyl silicate or TEOS), were more common than those intended for use on carbonated rocks (Winkler 1997; Gauri and Bandyopadhyay 1999; Illescas Salinas 2012). New products such as dibasic ammonium phosphate (DAP) are being tested to fill this gap and are showing good results in terms of stability and durability, as well as having no harmful effects on human health (Sassoni et al. 2011, 2012, 2013, 2015, 2016; Chelazzi et al. 2013; Molina et al. 2017).

With this in mind, in this paper we compare the effectiveness of two consolidants, one of which (TEOS) has been widely used for some time, while the other (DAP) appeared more recently. These products were tested on two varieties of sandstone, one of siliceous and the other of carbonate composition. The main objective of this study was therefore to assess the efficacy of each treatment with regard to the composition of the rock, in other words to find out whether the chemical affinity between the products and the rocks might affect their performance. To this end, we used samples of quarried stone and measured their different petrophysical properties (such as porosity, hydric behaviour, and changes in colour) before and after each treatment. The differences in the hydric behaviour between the two varieties of rock enabled us to assess the changes in the porous system; a fundamental aspect when analysing durability. We also measured the velocity of propagation of ultrasonic waves and the resistance to drilling. These measurements enabled us to determine the degree of consolidation and penetration of each product. Finally, in order to discover the efficacy of both treatments on each type of rock, we carried out a salt crystallization accelerated ageing test on the treated samples. We also bore in mind the orientation of the rocks so as to assess the influence of the fabric and/or the presence of laminations. The joint interpretation of the results will help us understand how the treated materials react when subjected to attack by salts and will provide very useful information for the conservator/restorer regarding the most suitable procedure to follow when working on these kinds of rock.

Materials and consolidant products

Stone building materials

There were many criteria involved in our decision to test the products on Arenisca Ronda and Molinaza Roja. The first was the fact that they have different chemical compositions, as this would allow us to compare the affinity of the selected consolidant products with regard to the two rocks with different compositions. Another interesting aspect was that both rocks were widely used in the architectural heritage of the cities of Ronda and Montoro (Andalusia, Spain) in historic buildings often several hundred years old (Clementson Lope 2012; Molina Piernas 2015), and that the same quarries are still in use today (Molina Piernas 2015). In spite of this, little research has been done on the characterization of these rocks and the factors influencing their decay (with a few exceptions—Clementson Lope 2012; Clementson Lope et al. 2007, 2009; Molina Piernas et al. 2011; Molina Piernas 2015; Molina et al. 2015), and even less work has been done to assess their degree of conservation and restoration. In our research, we decided to use non-weathered, “healthy” stones to better assess their behaviour when subjected to consolidation and to develop a knowledge base that would be useful in the study of real cases. Figure 1 shows their geographical location and the main causes of decay in real buildings (Fig. 1a, e). These rocks were therefore chosen in view of our intention to characterize them in petrophysical terms and assess the effectiveness of the consolidants for preserving the stone in good condition and to provide information to the conservator-restorer regarding the best procedure to follow in any restoration work.

Arenisca Ronda (AR) is associated with the infill in the basin of Ronda, one of the Neogene Post-Orogenic basins in the Betic Cordillera (Vera 2004). It is a Miocene calcarenite with a pinkish colour (Fig. 1b) made up of 98% calcite and the remaining 2% of quartz and phyllosilicates. In the clay fraction, we detected illite, chlorite, kaolinite and smectites (Molina Piernas 2015). In petrographic terms, it has abundant amounts of carbonated clasts (Fig. 1c, d) whose shape varies from oblong to sub-rounded, product of a process of reworking and with a size ranging between 100 µm and 1 mm, sometimes reaching as much as 2 mm. Fossil remains can only be found inside the micrite clasts. Cement is very abundant and is deposited between the gaps in the clasts, as well as filling the fissures. The porous system is clearly defined and associated with the processes of cementation and recrystallization that the rock has undergone. There are few interclastic pores, and they vary in size. Finally, we observed a slight orientation of the fabric due to sedimentary structures, identified in the quarry face as laminations (Molina et al. 2015). The quarries are situated about 7 km east-north-east of the city of Ronda (Málaga).

Molinaza Roja (MR) was deposited in a continental medium in fluvial and alluvial sedimentary environments during the Buntsandstein. It is a detrital sandstone, an arkose with pronounced lamination (Fig. 1f). The main mineral phase is quartz (70%), and it has varying percentages of feldspars (in the broadest sense of the term) and muscovite. Traces of calcite, dolomite, haematite and goethite can also be detected, the last two of which give the rock its characteristic reddish colour (Clementson Lope 2012; Clementson Lope et al. 2007, 2009; Molina Piernas et al. 2011). The mineral phases detected in traces are generally concentrated in the clayey matrix or in the carbonated or ferruginous cement (Molina et al. 2015). The clay fraction is composed of illite, kaolinite and chlorite. The quartz clasts are generally round or sub-rounded in shape and vary in size from 30 or 40 to 500 µm, the most representative value being 100–200 µm (Molina et al. 2015). The texture is clastic, and the banding is visible at macroscopic level (Fig. 1g, h). The origin of these clasts is metamorphous and igneous (Clementson Lope et al. 2009). The crystals of muscovite and sometimes of biotite altered to chlorite are generally orientated parallel to the lamination (Molina Piernas et al. 2011). Depending on the concentration of haematite and goethite, variations can be observed in the colour tone of the lamination, varying from light red to an intense shade of maroon. We identified three types of cement: ferruginous, carbonated and siliceous. The porous system is poorly defined and it is difficult to distinguish the pores, as they are small (between 10 and 40 µm) and scarce. It therefore appears to be a highly compacted rock (Molina et al. 2015). The quarry face is situated approximately 10 km west of the town of Montoro (Cordoba).

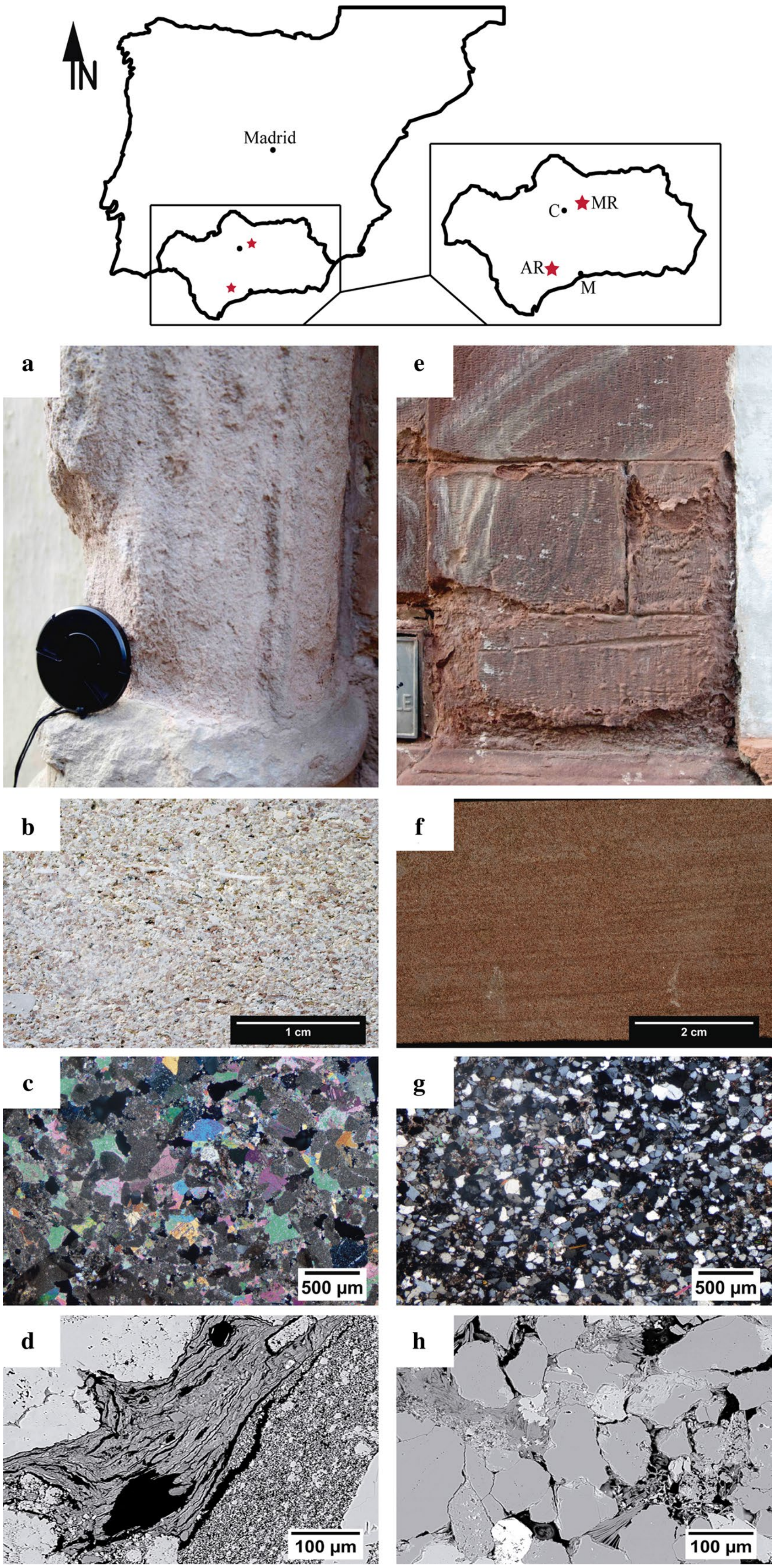
Consolidant products

Preparation of the consolidant products

The consolidant products selected for this research were ethyl silicate (TEOS) and dibasic ammonium phosphate (DAP), both of which are used in the consolidation of stone.

In the case of TEOS, the product used was WACKER OH 100, which is distributed by the German company Wacker Chemie AG. The manufacturer prepares the product with 75% of active ingredient, tetraethyl orthosilicate, diluted in White Spirit D40, and it is sold ready for use without any prior preparation. DAP is used as a precursor of calcium phosphates, frequently hydroxyapatite—HAP—as the last phase, and was supplied by the Sigma-Aldrich company. It is distributed in powder form with an active ingredient purity of 99%. The concentration of DAP used in this research was 2 M in distilled water, and to improve the homogeneity of the solution, we used a Bunsen analog magnetic stirrer series MC-8. We decided to use a concentration of 2 M of DAP on the basis of past research on this consolidant (Matteini et al. 2011; Sassoni et al. 2012, 2013, 2015; Franzoni et al. 2015b; Molina Piernas 2015), in which it was applied in concentrations of between 1 and 3 M.

Fig. 1 Location of the quarries of Arenisca Ronda (AR) and Molinaza Roja (MR). Close-up photographs showing the main processes of decay in AR (**a**) crumbling and scaling, and in MR (**e**) crumbling and blistering. Samples with visible details of the oriented fabric in AR (**b**) and of lamination in MR (**f**). Optical microscope images with crossed nicols showing the mineralogy and main textural aspects of AR and MR (**c** and **g**, respectively). SEM microphotographs showing the main decay processes in the two rocks, in AR due to swellable clays (**d**) and in MR due to a loss of cohesion between the clasts (**h**)



Methodology of application

Of all the various possible methods for applying the consolidant products (immersion, pulverization, paintbrush, poultice), we decided to use the paintbrush because it is one of the most frequently used methods by professionals working in the conservation and restoration of stone buildings and fittings (Durán Suárez 1996).

Before beginning consolidation, the surfaces of the non-weathered test samples were cleaned with distilled water, so as to eliminate any remains produced by cutting the rough quarry stone into 5 cm edge cubes. Later and after leaving them to dry in an oven at 50 °C for 48 h, the same amount of each product was applied in three coats with a paintbrush, impregnating the six faces of the cube samples. We waited for 40 min between each application, so as to make the test procedure as similar as possible to that used by conservation and restoration professionals. Although different methods of application could have been used on each stone, given the differences between their respective pore systems, we decided to use the same procedure in order to make it easier to compare the results; 5 days after application of the consolidants, we noticed that a whitish film appeared on the surface of the samples treated with DAP. We washed this film off with distilled water so as to eliminate any excess phosphate that might have been left behind without reacting.

Drying and polymerization conditions

The test samples treated with the consolidants were dried for a month so as to ensure that the products were polymerized. This was conducted in the laboratory under controlled relative humidity and temperature conditions (20% and 22 °C). Although DAP was shown to precipitate in just a few days (Sassoni et al. 2015; Molina et al. 2017), in the case of TEOS, polymerization took longer (Franzoni et al. 2015a). The samples were left to dry without covering them to prevent the evaporation of the solvent. Our aim in this case was to simulate a real situation in which it was impossible to cover the whole surface of the heritage piece being consolidated, such as for example the facade of a historical building.

When applying the products, we took into account the orientation of the fabric and of the sedimentary structures in the stone, given their involvement in the processes of decay of both rocks in real buildings (Fig. 1a, e). With this in mind, during the drying process, the test samples were oriented with these anisotropies perpendicular to the original sedimentation plane and were labelled as follows (AR-V_{DAP}, AR-V_{TEOS} and MR-V_{DAP}, MR-V_{TEOS}) so as to distinguish them from those dried and consolidated with parallel planes (AR-H_{DAP}, AR-H_{TEOS} and MR-H_{DAP}, MR-H_{TEOS}).

Analytical techniques

We used hydric tests to study the changes that took place in the porous system after application of the products in terms of the capacity of the two types of stone (treated and untreated) to absorb and expel the water and depending also on the orientation of their sedimentation planes (vertical or horizontal). Free absorption tests (A_b) were carried out in accordance with the UNE-EN 13755 (2008) standard and forced absorption (A_f) (RILEM 1980), and desorption (Normal 29/88 1988) tests were also performed. On the basis of these tests, we determined the drying index (D_i), saturation coefficient (S), the degree of pore interconnection (A_x) (Cultrone et al. 2003), the real (skeletal) (ρ_{sk}) and apparent (bulk) density (ρ_b) and open porosity values (P) (UNE-EN 1936 2007). We used 12 test samples of Arenisca Ronda and 12 of Molinaza Roja. Six of the 12 samples were treated with dibasic ammonium phosphate (DAP) and the other six with ethyl silicate (TEOS). Of these, three were positioned with their sedimentation planes perpendicular to the surface and the other three were positioned parallel to it. The temperature (25 °C) and relative humidity (30–40%) in the laboratory were controlled at all times.

In order to measure the degree of compactness of the treated and untreated samples, we used a Parametrics HV Pulser/Receiver 5058 PR coupled to a Tektronix TDS 3012B oscilloscope, with which we measured the velocity of ultrasonic wave propagation (V_P) using 1 MHz transducers. In order to ensure a homogeneous contact between test sample and transducers, we applied a gel on the surfaces we were measuring. The P-waves were recorded by positioning the transducers using the direct method, according to the UNE-EN 14579 (2005) standard, measuring the velocities in each of the three mutually perpendicular directions of each test sample. Once all the data had been obtained, we then calculated the relative anisotropy (Δm_P) and total anisotropy (ΔM_P) values (Guydader and Denis 1986).

Resistance to drilling was measured using a DRMS Cordless Drill (Sint Technology) equipped with a 5-mm-diameter bit with a flat edge and a diamond-covered tip. The working conditions were as follows: velocity of revolution = 600 rpm, penetration rate = 10 mm/min and hole depth = 5 mm. The measurements were controlled using a calibration standard to correct the possible deviations due to wear of the bit. The results were later standardized with regard to the diameter of the drill bit (Pamplona et al. 2007).

Spectrophotometry was used to quantify the colour of the stone before and after application of the consolidant, so as to assess any changes in accordance with the UNE-EN 15886 (2011) standard and using a Minolta CM-700d spectrophotometer equipped with a xenon lamp and a geometry of diffuse reflectance.

The measurement conditions were as follows: spot diameter of 8 mm, specular component in SCI mode (this mode measures both the light reflected specularly and the light reflected diffusely), wavelength range from 360 to 740 nm with an interval of 10 nm, an angle of 10° and a D65 illuminant, which corresponds to daylight with a colour temperature of 6504 K. The difference in colour (ΔE^*) was calculated using the following equation (UNE-EN 15886 2011):

$$\Delta E = \sqrt{\left(L_2 - L_1\right)^2 + \left(a_2 - a_1\right)^2 + \left(b_2 - b_1\right)^2}$$

where L_1, a_1 and b_1 are the lightness and chromaticity values for the untreated samples and L_2, a_2 and b_2 are those for the treated samples.

In order to study the resistance of the rock to decay agents and to evaluate the efficacy and durability of the consolidation treatment, we performed the salt crystallization accelerated ageing test, as this is one of the most frequent types of decay affecting the durability of rock (López-Arce 2012).

For this test, we aged the 24 consolidated test samples used previously in the hydric tests. In order to facilitate the visualization of fragment loss, the edges were labelled with a marker pen. Those treated with dibasic ammonium phosphate were labelled with a black pen and those treated with ethyl silicate with a blue one. We also took the orientation of the sedimentation planes into account, marking them with a red cross when the planes were positioned perpendicular to the original stratification. This test was conducted in accordance with the UNE-EN 12370 (2002) standard. Fifteen test cycles were performed using a solution of sodium sulphate decahydrate ($NaSO_4 \times 10H_2O$) at 14%. The test samples were tested by total immersion and placed on top of a grille, so as to enable the salt to penetrate into all six sides of the cube. At the end of each cycle, the change in weight of the test samples was recorded. The test was performed in the laboratory under controlled temperature (20 °C) and relative humidity (25–30%) conditions.

Results and discussion

Hydric behaviour of the stone samples

The results of the hydric tests to assess possible changes in the porous system after application of the consolidant are set out in Fig. 2 and Table 1.

The hydric behaviour of both kinds of untreated rock showed a similar pattern to that described in previous research (Molina et al. 2015); in other words, AR absorbs more water (A_b and A_f in Table 1 and Fig. 2I) and shows a degree of pore interconnection that was slightly worse than MR (A_x, Table 1 and Fig. 2II). We could not find any differences as regards the orientation of the samples (H_NT or V_NT, Fig. 2), except in the desorption phase (Fig. 2III), in which the samples in which the clasts are oriented parallel to the base (H_NT) took longer to finish the test. In the AR samples, we noticed some differences in the drying, due possibly to the water retained by the swellable clays (smectites) contained in this rock.

The application of the consolidants had a direct impact on the hydric behaviour of the rocks, as can be seen in Fig. 2 (*T* samples) and in the data in Table 1 (*T* samples). There are some differences depending on the type of consolidant applied. In the case of AR, the curve for free water absorption (I) shows that after application of the TEOS, there is a smaller increase in mass over the first 24 h. This means that a degree of resistance to water absorption has been produced thanks to the hydrophobic effect of the consolidant (Franzoni et al. 2015a), although we later observed that this effect was temporary. In addition, in the samples treated with DAP there is practically no difference at all compared to the untreated sample, with an increase in the absorption rate of less than 0.01%. By contrast, during the forced water absorption test (II) and the free desorption test (III), AR samples treated with TEOS behave in almost identical fashion to those treated with DAP, although desorption seems quicker in the treated samples. In an attempt to explain this behaviour, we analysed the A_x and D_i (Table 1) values. According to these parameters, the degree of pore interconnection (A_x) improves considerably after consolidation, which means that the consolidants are probably filling small, poorly connected pores. However, even if the treated stones appear to dry faster, at the end of the test all the samples had very similar drying index (D_i) values, values that consider the integral of the whole drying curve.

Propagation of ultrasound waves

Arenisca Ronda (AR) had the highest velocity value (V_P) in healthy samples not subjected to the ageing test (Fig. 3). This was due above all to its mineralogical composition, as calcite propagates the waves more quickly (approx. 6660 m/s) than quartz (approx. 5800 m/s) (Carmichael 1989). It was not related to its porosity since the *P* value was either quite similar or slightly higher in AR than in MR (Table 1). We obtained lower values than those indicated in the bibliography due to the texture of the rocks (grain boundaries, porosity, sedimentation planes, etc.) and the presence of other mineral phases (feldspars, phyllosilicates, etc.).

Both rocks, characterized by the presence of textural anisotropies (orientation of the clasts and lamination), show a change in the velocity in three measured spatial directions (V_{P1}, V_{P2}, V_{P3}; NT-Fig. 3). In general, the direction with the lowest velocity value was V_{P1} in that the waves propagated perpendicular to the lamination, while the highest value V_{P3} coincided with the orientation of the

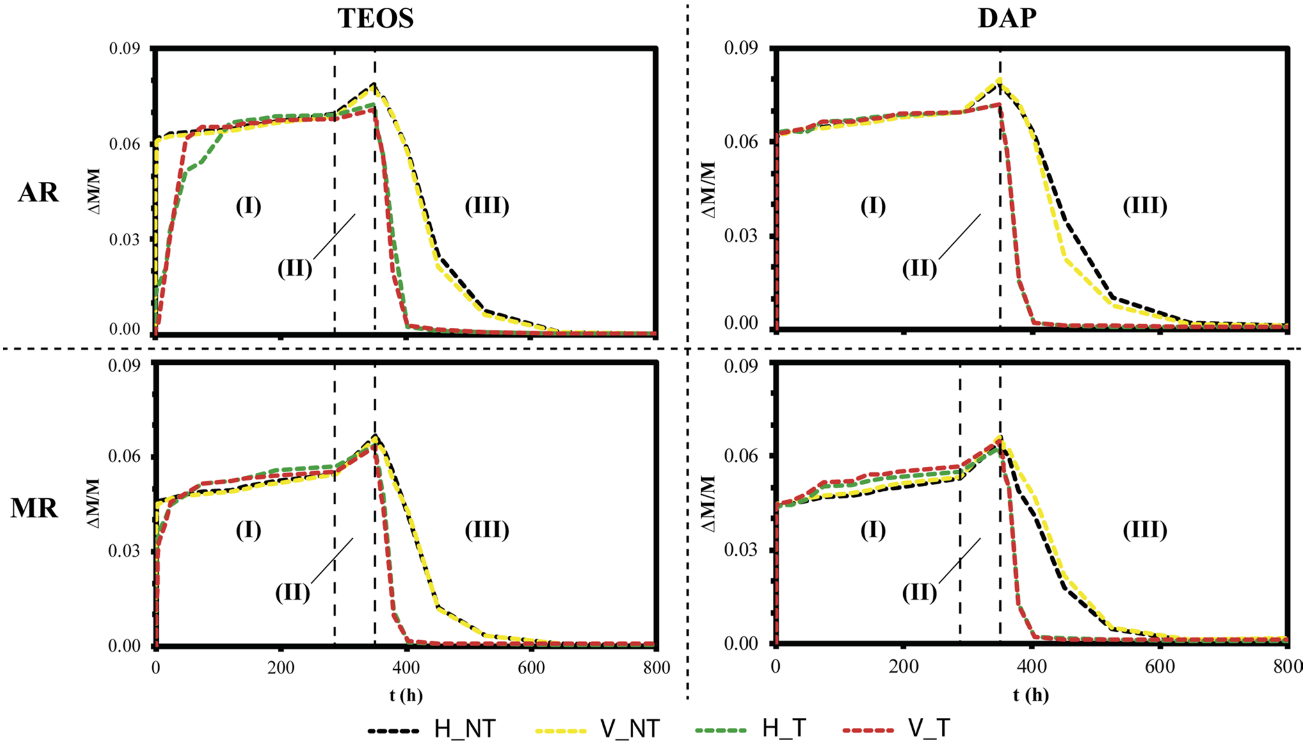


Fig. 2 Curves for free absorption of water (I), forced absorption (II) and desorption (III) in Arenisca Ronda (AR) and Molinaza Roja (MR). Variation in weight (ΔM/M) over time (t, in h). *TEOS* ethyl silicate, *DAP* dibasic ammonium phosphate, *NT* untreated samples, *T* treated samples, *H* sedimentation planes parallel to the base surface, *V* sedimentation planes perpendicular to the base surface

Table 1 Characterization of the hydric behaviour of Arenisca Ronda (AR) and Molinaza Roja (MR) in untreated (NT) and treated (*T*) samples taking into account the orientation of the sedimentation planes in which "V" indicates an orientation perpendicular to the surface of the base and "H" a parallel orientation. The initials TEOS and DAP refer to the consolidant products applied, namely ethyl silicate and dibasic ammonium phosphate

	P		ρ_b		ρ_{sk}		A_b		A_f		A_x		S		D_i	
	NT	T	NT	T	NT	T	NT	T	NT	T	NT	T	NT	T	NT	T
AR-H_{TEOS}	20.9	18.9	2.21	2.20	2.66	2.62	6.93	6.89	7.85	7.23	11.6	4.64	80.9	71.6	0.94	0.94
AR-V_{TEOS}	22.1	18.5	2.34	2.21	2.86	2.62	6.81	6.79	7.75	7.07	12.1	3.98	81.3	86.7	0.94	0.94
AR-H_{DAP}	21.0	18.8	2.19	2.19	2.66	2.61	6.93	6.93	7.89	7.19	12.2	3.53	81.2	87.7	0.94	0.94
AR-V_{DAP}	20.8	18.8	2.16	2.19	2.61	2.60	6.94	6.93	8.00	7.20	13.3	3.74	80.3	89.3	0.94	0.94
MR-H_{TEOS}	17.5	14.3	2.24	2.30	2.63	2.61	5.45	5.68	6.69	6.37	18.5	10.9	71.6	75.8	0.96	0.94
MR-V_{TEOS}	17.2	14.1	2.24	2.24	2.63	2.61	5.43	5.50	6.57	6.31	17.3	12.2	72.3	76.7	0.96	0.94
MR-H_{DAP}	16.9	14.0	2.25	2.24	2.63	2.62	5.29	5.51	6.43	6.27	17.7	12.0	71.1	73.3	0.96	0.94
MR-V_{DAP}	17.7	14.5	2.28	2.23	2.69	2.62	5.33	5.68	6.59	6.46	19.1	12.0	70.3	74.0	0.96	0.94

P open porosity (%), ρ_b apparent density (g/cm^3), ρ_{sk} real density (g/cm^3), A_b absorption of water at atmospheric pressure (%), A_f absorption of water in a vacuum, A_x degree of interconnection between the pores, D_i desorption index, S saturation coefficient (%)

fabric, so manifesting the preferential orientation of the clasts in both AR and MR. This fact is reinforced by the anisotropy values (ΔM and Δm, Table 2), which are very similar in both AR and MR, so confirming the textural heterogeneity and the pronounced orientation of the fabric of both rocks. This pronounced anisotropy means that the rocks have a particular direction that is more likely to suffer damage, as can be seen in real buildings.

The difference in velocity between the untreated (NT) and the treated (*T*) samples is evident, as in both AR and MR the velocity of propagation of the P-waves increased in the three directions we measured (V_{P1}, V_{P2}, V_{P3}, Fig. 3), regardless

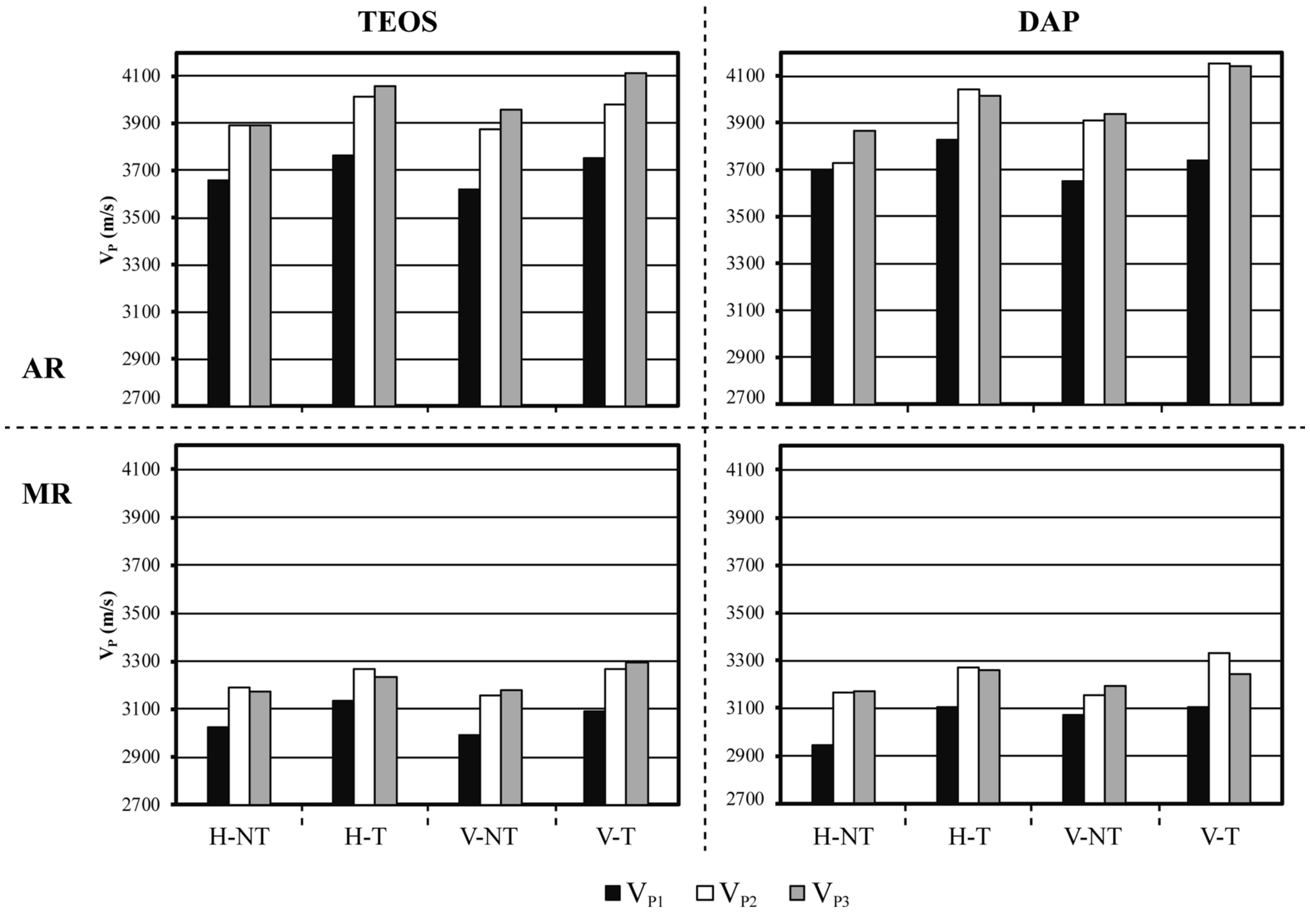


Fig. 3 Change in the P-wave velocity (V_P, en m/s) of Arenisca Ronda (AR) and Molinaza Roja (MR) in untreated samples (NT) and samples treated (*T*) with ethyl silicate (TEOS) and dibasic ammonium phosphate (DAP), taking into account the orientation of the sedimentation planes relative to the base surface: H, sedimentation planes parallel to the base surface; V, sedimentation planes perpendicular to the base surface

of the type of consolidant used. This increase in velocity suggests that the treatments have precipitated, filling the porous space near to the surface. On this question, Molina and Cultrone (2014) observed that consolidation with DAP caused a modification in pore size distribution and a reduction in porosity in AR and MR stones. The penetration of

Table 2 Average values for the velocity of P-wave propagation and of anisotropy of the Arenisca Ronda (AR) and the Molinaza Roja (MR) of untreated (NT) and treated (*T*) samples taking into account the orientation of the sedimentation planes in which "V" indicates an orientation perpendicular to the surface of the base and "H" a parallel orientation. The initials TEOS and DAP refer to the consolidant products applied, namely ethyl silicate and dibasic ammonium phosphate

	V_P		ΔM_p		Δm_p	
	NT	*T*	NT	*T*	NT	*T*
AR						
AR-H_{TEOS}	3813	3945	5.97	6.77	0.12	1.06
AR-V_{TEOS}	3818	3946	7.53	7.22	2.09	3.31
AR-H_{DAP}	3763	3961	2.58	5.06	3.65	0.64
AR-V_{DAP}	3835	4011	6.91	9.76	0.63	0.19
MR						
MR-H_{TEOS}	3130	3212	4.93	3.47	0.56	1.04
MR-V_{TEOS}	3109	3217	5.61	5.76	0.63	0.79
MR-H_{DAP}	3093	3212	7.13	4.81	0.31	0.30
MR-V_{DAP}	3142	3227	3.21	5.61	1.2	2.7

V_P velocity of propagation of P-waves in three mutually perpendicular directions (in m/s), ΔM_p total anisotropy coefficient (%), Δm_p relative anisotropy coefficient (%)

the products due to the characteristics of the porous system seems therefore sufficient to demonstrate the effectiveness of the application by paintbrush. Finally, no relation could be observed between the compositional affinity of the rock and the treatment given the similar values in ultrasounds.

Resistance to drilling

Figure 4 shows the drilling resistance values versus the depth of penetration of the drill (R_D). Firstly, we observed that the results for the untreated healthy samples of MR (values for each rock measured without taking the orientation of the fabric, NT, into account) are higher than those for AR, due undoubtedly to the different mineral composition, given that quartz, the dominant mineral phase in MR, is more resistant to abrasion than calcite, the main component of AR.

After treating the samples, in AR we noticed a general increase in the drilling resistance value regardless of the type of consolidant product used, although it is important to make clear that the application of TEOS has resulted in higher values than those obtained with DAP (Fig. 4-AR). This difference was greater in perpendicular direction to the main orientation of the fabric (AR-V_{TEOS}). TEOS seems to be more effective as regards performance at depth, given that the increase in resistance is greater and more constant down to 5 mm (depth limit of this analysis) compared to DAP, which acted up to a depth of 2.5–3 mm, from which point the resistance value decreases, reaching almost as low as the values for untreated rock. In the case of MR, the treated samples show generally lower R_D values than the untreated samples and the samples treated with TEOS are more resistant than those treated with DAP (Fig. 4-MR). The exception to this trend is MR-H_{DAP} which has much higher drilling resistance than the other samples. After the first 1–2 mm, there is a decrease in resistance, but it still remains higher than the others. This was due to the high level of heterogeneity of MR, which made it impossible to carry out the test correctly. This means that the drilling results, above all for MR samples, are not totally reliable and must be assessed with a degree of caution. Molina Piernas (2015) demonstrated that there is an important contribution to the resistance provided by the amount of cement/matrix present and that it is not evenly distributed within the rock. In any case, we can observe that between 1.5 and 2 mm from the surface there is a slight increase in the resistance with regard to the untreated samples, which would indicate that the two products definitely act up to depths of 2 mm.

In general, there is a slight difference as regards the resistance to drilling caused by the orientation of the fabric, something that was most evident after application of TEOS. The vertical layout of the sedimentary structures undoubtedly favours the penetration of the product, something which is aided by the absorption capacity of these rocks.

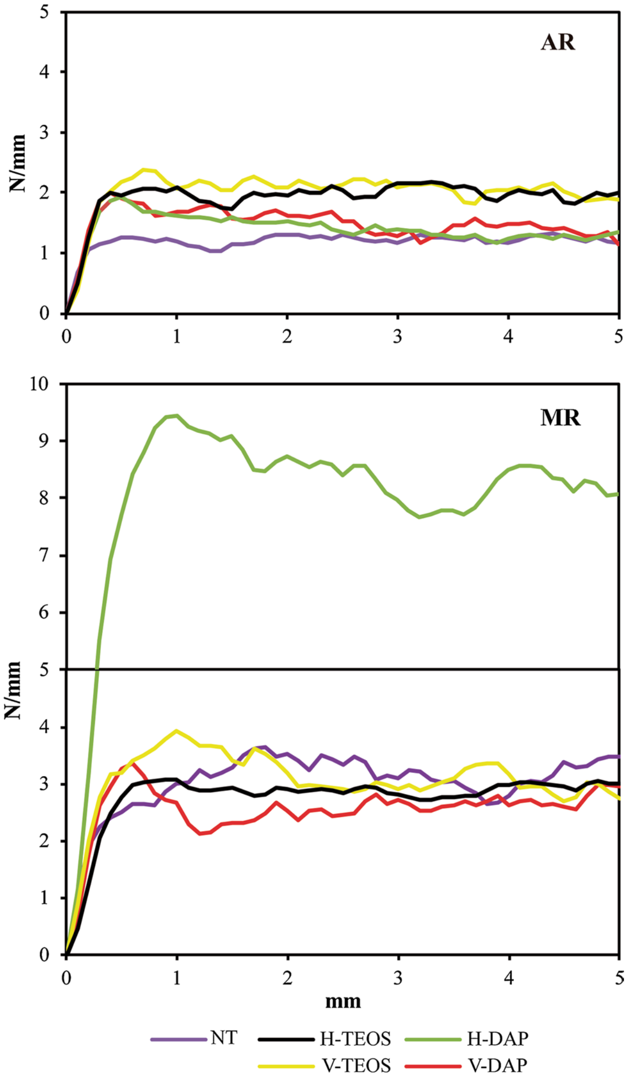


Fig. 4 Drilling resistance (R_D) curves for untreated (NT) and treated samples (T) of Arenisca Ronda (AR) and Molinaza Roja (MR) depending on the orientation of the sedimentation planes relative to the direction of penetration of the drill bit. H, sedimentation planes parallel to the base surface; V, sedimentation planes perpendicular to the base surface

Variation in colour

Table 3 shows the spectrophotometry results for the samples before (NT) and after treating (T) them with consolidants.

A slight change in colour can be observed with the naked eye in the samples treated with DAP. This is most obvious in Molinaza Roja as a result of the appearance of a thin crust produced by the precipitation of calcium phosphates. The spectrophotometry data confirm the change in colour with a drop in the lightness values in both lithotypes and regardless of the type of consolidant product applied. In all the samples except one, the difference in colour (ΔE^*) was over 5 units, which means that the human eye may be able to notice a

Table 3 Spectrophotometry measurements in untreated (NT) and treated (*T*) samples of Arenisca Ronda (AR) and Molinaza Roja (MR). The initials TEOS and DAP refer to the consolidant products applied, namely ethyl silicate and dibasic ammonium phosphate

	NT			*T*			
	*L**	*a**	*b**	*L**	*a**	*b**	Δ*E**
AR							
TEOS							
Φ (σ)	77 (8.7)	5 (1.1)	14 (2.6)	72 (0.9)	6 (0.5)	14 (1.3)	5.09
Max–min	81–74	7–2	16–11	74–71	5–7	13–16	
DAP							
Φ (σ)				74 (1.3)	5 (0.6)	11 (1.3)	9.11
Max–min				76–72	4–6	10–14	
MR							
TEOS							
Φ (σ)	58 (7.3)	9 (1.2)	14 (1.8)	54 (2.7)	9 (0.9)	12 (1.5)	4.47
Max–min	66–54	11–7	16–12	57–51	9–11	7–13	
DAP							
Φ (σ)				49 (1.8)	10 (0.5)	13 (1.4)	9.13
Max–min				52–47	9–11	10–14	

*L** Lightness, *a* and b** chromatic parameters, Δ*E** colour difference. In the table, we can see the average value (Φ), the standard deviation (σ) and the maximum and minimum values obtained from 24 measurements of each sample

difference in colour between the treated and untreated rocks (Grossi et al. 2007). This means that the colour difference is significant and is accentuated in the samples treated with DAP in which there are some difference values of more than 9 units compared to the healthy samples. The high ΔE values measured in both sample types treated with DAP are probably related to the specific product concentration, application procedure and types of stones investigated.

Effectiveness of the consolidant treatments against salt crystallization

Molina et al. (2015) demonstrated that these rocks suffer substantial damage after the crystallization of sodium sulphate inside them, above all in the AR samples in which there is a significant loss of material due to sanding, flaking and blistering (Vergès-Belmin 2008) due, at least in part, to the presence of swellable clays (e.g. Figure 1d) and the orientation of the fabric. This test did not enable us to determine to what extent the presence of smectites could have influenced the decay process. In the case of MR, the damage is manifested in the form of powdering/sanding (Vergès-Belmin 2008) due to the loss of cement and matrix, and in some cases, the test samples split along the lamination planes (delamination processes) (Vergès-Belmin 2008) (Fig. 1h). This is why in our research we performed the ageing test after applying the consolidant treatment and could therefore evaluate the behaviour of both rocks according to the particular treatment applied and the orientation of the fabric.

The results of this test are set out in Figs. 5, 6 and 7. Two different states can be distinguished in the behaviour of the rocks: in the first stage (cycle 1 to 6–8), the salt is deposited in the porous system, which results in an increase in weight regardless of the consolidant used. By contrast, the second stage (cycle 8 to the end) is characterized by the loss of material and in consequence, the loss of weight, which is much more pronounced in the AR samples than in MR (Fig. 5).

The damage varied according to the different treatments, and for this test, a certain correlation could be observed between the composition of the rock and that of the product. On this basis, we observed that the AR samples treated with DAP have lost less material than those treated with TEOS, while the opposite is true of the MR samples. The correlation between the loss of weight and the damage is quite evident to the naked eye. In the case of AR (Fig. 6), we observed two main patterns of decay. The first is characterized by a scaling in line with the sedimentation planes and the orientation of the clasts, as can be observed in samples H-DAP, V-DAP and V-TEOS. The second type of damage took place in the H-TEOS samples, in which it was very clear how far the consolidant had penetrated, as there was a similar loss of material on all sides of the sample up to a depth of approximately 4–5 mm. This limit was already indicated by the measurement of the drilling resistance in most of the samples we analysed. At the same time, it should be borne in mind that the most aggressive effects of this test take place at just a few millimetres from the surface (Benavente et al. 2004; Espinosa et al. 2001). The progress of the decay is also enhanced by the characteristics of the porous system and the presence of pores of less than 1 µm in size (Everett 1961). In the final cycles of the accelerated ageing test, we observed that the propagation of the fractures

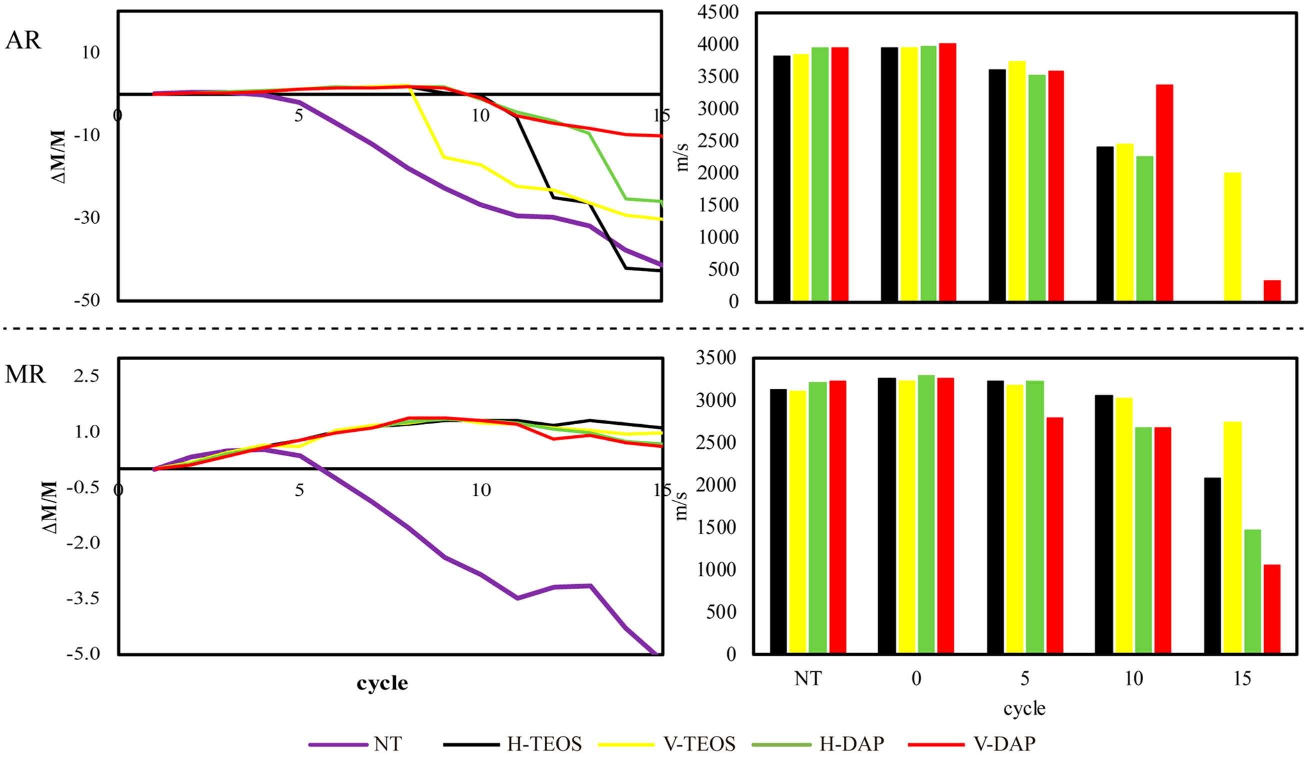


Fig. 5 Change in weight (Δ*M*/M) during the salt crystallization test and the P-wave velocity (V_P, in m/s every 5 cycles) measured in Arenisca Ronda (AR) and Molinaza Roja (MR) untreated samples (NT), and treated with ethyl silicate (TEOS) and dibasic ammonium phosphate (DAP), bearing in mind the orientation of the sedimentation planes relative to the base surface. V signifies a perpendicular orientation and H a horizontal one

in the same direction of the oriented clasts and even in different directions is frequent, causing the total disintegration of the samples, regardless of the product used. The damage that takes place in the laboratory samples is very similar to that observed in real cases (Fig. 1a). Although it did not prevent complete disintegration of the samples, the application of the products did manage to delay the onset of decay compared to the results obtained by Molina et al. (2015). This finding must be taken into account when performing restoration work on this material.

In addition, the damage suffered by the MR samples (Fig. 7) is manifested above all in the crumbling of the surface of the samples and the appearance of cracks along the sedimentation planes. However, the samples of this rock remain more intact than those of AR up to practically cycle 10. From that point onwards, the surface begins to undergo a process known as blistering (Fig. 7, cycle 10).

Finally, the velocity of propagation of the P-waves, which was measured every 5 cycles, is shown in Fig. 5. This test confirms the gradual process of decay that takes place in both rocks. In AR, we also observed that from cycle 10 onwards, there is a strong attenuation of the signal due to the significant development of fissures and poor cohesion between the clasts, which begins in the part nearest the surface and gets deeper with each cycle, to the point that measurement becomes impossible during the last cycles. As regards MR, a very gradual reduction in velocity was recorded right from the beginning of the test. This reduction was due to the crumbling of the surface, and the opening up of fractures inside the samples, a fact that was manifested towards the end of the test by the appearance of fissures favoured by the lamination planes, to such an extent that some of the samples completely disintegrated (Fig. 7, cycle 15).

Conclusions

The results obtained in our research indicate that it is important to take into account the affinity between the composition of the consolidant product and that of the rocks, when choosing the most suitable consolidant product. The tests carried out revealed that the dibasic ammonium phosphate (DAP) obtains better results for the Arenisca Ronda, a rock whose main mineral phase is calcite, while the ethyl silicate (TEOS) behaved better with Molinaza Roja, due to the silicic composition of their mineral components. In addition, the decision to apply the

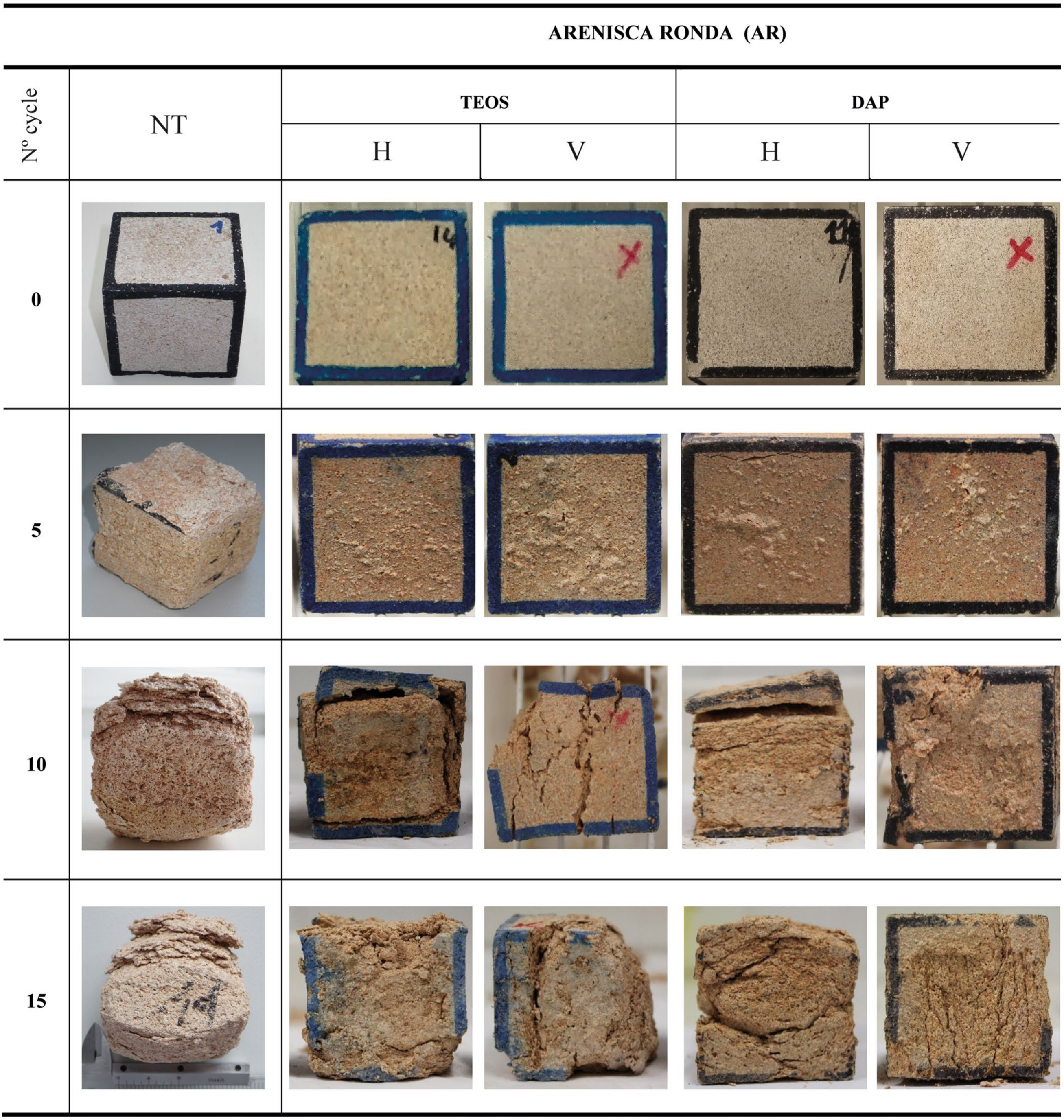


Fig. 6 Visual appearance of the samples of Arenisca Ronda (AR) before and during the salt crystallization test, as seen at the beginning of the test (no cycle = 0) and every five cycles (cycles 5, 10 and 15). The figure shows untreated (NT) and treated 5 cm edge cubic samples with ethyl silicate (TEOS) and dibasic ammonium phosphate (DAP), taking into account the orientation of the sedimentation planes relative to the base surface. V signifies a perpendicular orientation and H a horizontal one

product by paintbrush and the methodology used (three applications every 40 min completely impregnating the surface) provide acceptable results in both rocks, given that the consolidant products have homogenously penetrated between 2 and 5 mm beneath the surface.

As regards their hydric behaviour, both consolidants have improved the desorption inside the porous system. The time elapsed between the application and the polymerization of the consolidants until the beginning of the hydric tests (1 month) was sufficient to ensure that the products worked

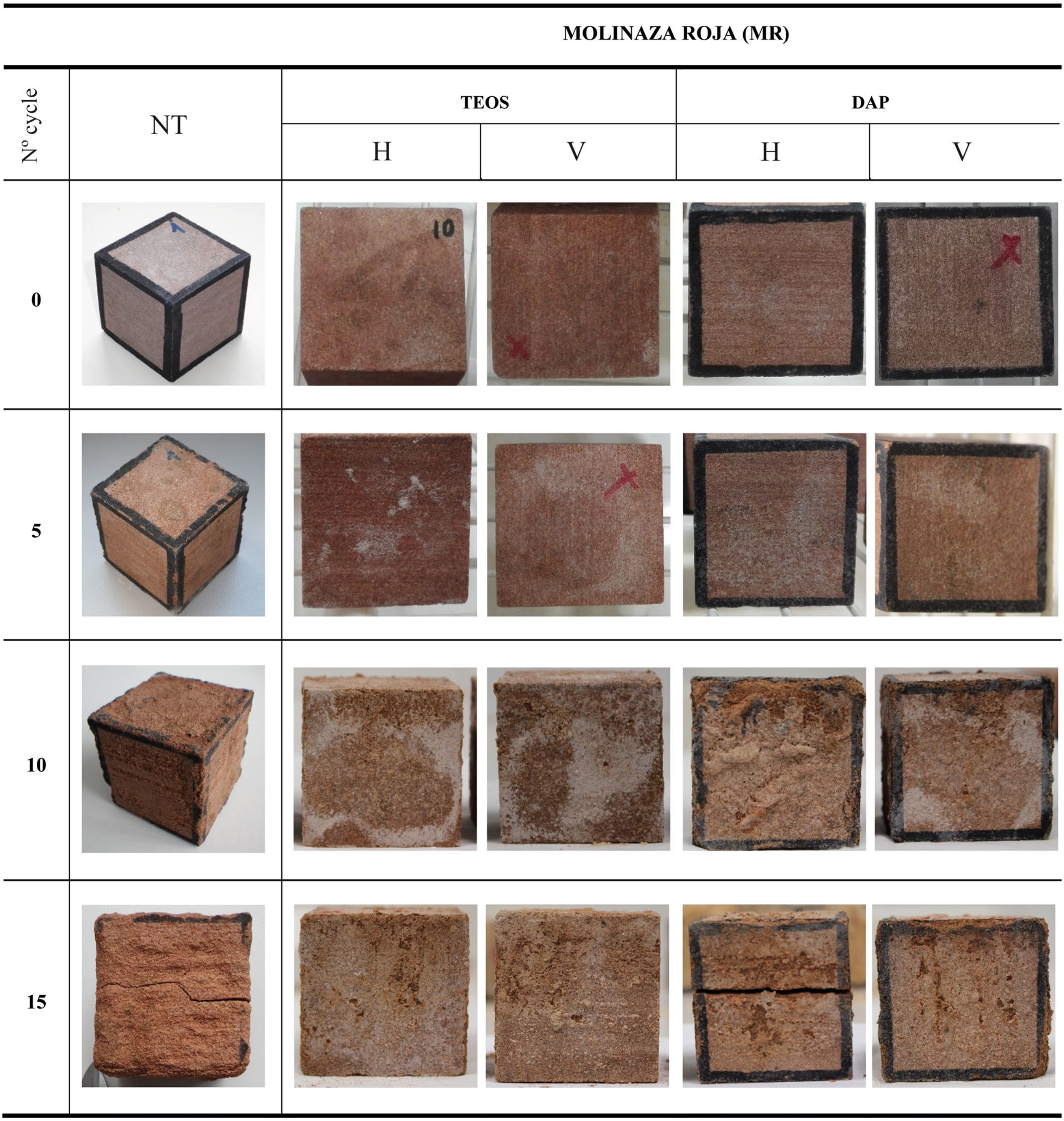


Fig. 7 Visual appearance of the samples of Molinaza Roja (MR) before and during the salt crystallization test, as seen at the beginning of the test (no cycle = 0) and every five cycles (cycles 5, 10 and 15). The figure shows untreated (NT) and treated 5 cm edge cubic samples with ethyl silicate (TEOS) and dibasic ammonium phosphate (DAP), taking into account the orientation of the sedimentation planes relative to the base surface. V signifies a perpendicular orientation and H a horizontal one

properly. In addition, the results for the velocity of ultrasonic P-waves before and after application showed an increase in the velocity of the P-waves, so confirming that polymerization had taken place.

The results in terms of visual appearance are not so positive, as the application of the consolidant resulted in a difference in colour in excess of the minimum levels detectable by the naked eye ($\Delta E \geq 5$). This colour difference was greater when dibasic ammonium phosphate (DAP) was used, in some cases reaching levels of more than 9. When the hydroxyapatite precipitates, a slight crust is formed on the surface. In order to minimize this drawback, we propose the application of cellulose pulp poultices with demineralized water, placing a piece of Japanese tissue paper between the surface of the rock and the poultice, so as to try to eliminate or reduce this fine superficial layer. However, one drawback in this method could be the incipient swelling of smectites in Arenisca Ronda due to the presence of water in the cellulose pulp poultice. It is therefore necessary to continue research on this question so as to avoid this undesired crust from appearing on the surface, exploring alternative methods of application.

The vertical or horizontal alignment of the fabric or of the laminations present in the rocks has not influenced the results as might be expected, either in terms of the penetration of the consolidant or of the damage produced. Nonetheless, we did observe that the damage was delayed in the samples of Arenisca Ronda and minimized in those of Molinaza Roja, as compared to the untreated samples. For this reason, the preventative application of these treatments on the basis of the mineral composition of each type of rock could improve their protection and in the event that decay has already started, slow down the decay process. Moreover, in view of the presence of swellable clays in Arenisca Ronda, swelling inhibitors should be tested before consolidation treatment in order to improve stone durability.

Finally, it is important to emphasize the need to make preliminary studies of both the stone being treated and the products being used. The time required for the total polymerization of the product must also be taken into account, given that consolidants that take a long time to polymerize could be counterproductive for the protection of the historical building.

Acknowledgements This study was financially supported by Research Group RNM179 of the Junta de Andalucía and by Research Project MAT2016-75889-R. We are grateful to Nigel Walkington for his assistance in translating the original text.

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