Consolidation of carbonate stones: Study of the potential compatibility of alkoxysilane-based treatments

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Abstract

The dissertation aims to contribute to the evaluation of the potential compatibility of consolidation treatments performed on two carbonate varieties with an important presence in the Portuguese Patrimony, Trigache marble and *Pedra de Ançã*, which have very different characteristics although chemically predominantly constituted of calcite.

These treatments resulted from application of consolidating products based on alkoxysilanes and an inorganic product (ammonium phosphate) until the apparent saturation of the supports and until the liquid fringe reached 10mm depth. Brushing was the procedure used in both types of treatment studied on sound stone (*Pedra de Ançã*) and artificially degraded stone (marble).

The study of the potential compatibility of consolidation treatments was supported on the characterization of the stone materials, before and after their treatment, and was based on a multi-criteria methodology that considered the changes promoted by the treatments in the properties related to water transport, in the color of the stone materials' surfaces and also in their tendency to develop superficial hard crusts in *Pedra de Ançã*.

All the studied products revealed an evident higher potential of incompatibility when applied to the *Pedra de Ançã* than to the marble, reinforcing the risks and difficulties that have been reported in consolidating very porous limestones. In global terms, the treatments with the product BS-OH were the ones that revealed the highest degree of incompatibility, followed by the treatments with the product HCl.PEG, while the treatments with the product HCl.nSiO_2 were the ones that showed the lowest degree of incompatibility among all the products.

Keywords: Portuguese Heritage, Marble, Limestone, Consolidation Treatments, Compatibility.

1. Introduction

Since the 1st century BC, carbonate stones in Portugal have been extensively used for the construction of fortifications, historical monuments, and decorative elements with specific and particular values recognized by the community, which need to be preserved and conserved (Casal Moura, 2007). Two varieties of carbonate stones that are widely present in Portuguese patrimony are marble (Temple of Diana in Évora, the Ducal Palace in Vila Viçosa, and the Roman Villa of Pisões in Beja (Fusco & Romero, 2006)) and limestone (Jerónimos Monastery, Queluz Palace in Lisbon, and Santa Cruz Church in Coimbra (Trindade *et al.* 1998)).

The stones used in the patrimony are considered durable, however, they are susceptible to various phenomena that cause their degradation, such as the intrinsic properties of the stones, the environment, and the constructions (Delgado Rodrigues, 1989). The knowledge of the forms and mechanisms of degradation of the stony varieties is determinant for the selection of the conservation action to be performed, for instance, in the case of marble the main degradation mechanism is temperature variations and in porous limestones, it's salt crystallization.

The use of consolidation treatments, i.e. the application of a given consolidating product according to a specific procedure, should only be considered for conservation actions when it is essential to protect a surface that is at risk of imminent loss (or in the process of loss) (Delgado Rodrigues, 2003). A consolidation treatment aims at re-establishing the cohesion of the degraded stone material, which means, that the application of the consolidating product must be able to increase the mechanical characteristics of the object being treated; the study of the potential initial efficacy may use drilling resistance tests (DRMS) and ultrasonic velocity (Costa & Delgado Rodrigues, 2012). Besides the initial effectiveness, the study and selection of a consolidation treatment needs to include the evaluation of its potential compatibility and durability, with the objective of trying to ensure that its application will not be responsible for accelerating or aggravating the degradation of the stone object being treated, as well as, that it manifests a satisfactory susceptibility to degradation that indicates durability that justifies its application.

The assessment of the compatibility of a consolidation treatment seeks to ensure that the material treated presents characteristics as close as possible as of the sane material, ideally identical, to ensure that the treatment will not trigger significant changes, such as aesthetic changes visible to the human eye or the alteration of other physical and mechanical properties. The undesirable effects that may arise from a poorly compatible consolidation treatment may lead to the total or partial loss of numerous elements of high value, as they potentiate the acceleration of their degradation (Delgado Rodrigues & Grossi, 2007).

To evaluate compatibility, Delgado Rodrigues and Grossi (2007) proposed a multi-criteria system that allows the quantification of the potential risk of incompatibility of a consolidation treatment based on the variation of the properties of the treated and untreated support. The methodology encompasses several criteria that are subdivided into compatibility indicators that in turn are classified according to the incompatibility risk. The integration of information on the quantification of the incompatibility risk allows an overall assessment of the consolidation treatment to be obtained through the degree of incompatibility.

2. Materials and methods

2.1. Stone materials

For the experimental campaign, two carbonate stone varieties were selected with a presence in the Portuguese heritage but have different properties. Trigaches marble and *Pedra de Ançã* (porous limestone) are from two quarry areas located in Portugal, Trigaches and Cantanhede, respectively.

The Trigaches marble was submitted to an artificial degradation process by thermal action in order to obtain similar characteristics to degraded marbles, according to the procedure detailed in document (Sena da Fonseca et al. 2021[1]). The samples of *Pedra de Ançã* came from two blocks (Block A2 and Block A6) which had similar characteristics, and the tests were performed using healthy samples.

Table 1 are presented some properties of the carbonated stones under study. It can be observed that the water absorption coefficient of the marble samples presents much lower values than the samples from *Pedra de Ançã*. Regarding the drying index and water vapor permeability, the values for both stone materials are within the same order of magnitude.

Tabela 1 – Some basic properties of the select stones (n=number of samples).

Stone material	Designation		Dimensions	WAC		DI		RC	
				n	$[\times 10^{-3}\ kg/m^2.s^{1/2}$	n	$[\times 10^{-3}\ kg.h^2/m^2]$	n	$[\times 10^{-8}\ kg/Pa.h.m$
Trigaches Marble	Marble	Sound	4x4x3 cm	2	1,9±0,1	2	9,0±0,5	2	1,5±0,1
		Decayed		3	8,9±1,4	3	7,6±0,5	3	2,1±0,3
Pedra de Ançã	Block A2	Sound	3x3x3 cm	3	142,8±2,2	3	12,3±0,4	3	2,3±0,1
	Block A6	Sound	4x4x4 cm	3	114,3±7,5	3	8,6±0,6	3	3,0±0,7

WAC – water absorption coefficient; DI – drying index; RC – water vapour permeability.

2.2. Stone consolidants and treatments

2.2.1. Stone consolidants

Table 2 – Details about the consolidants products (adapted Sena da Fonseca et al. 2021[2])

Consolidants products	Type	Description
BS OH	Alkoxysilane	Commercial product Wacker Silres BS OH (neutral catalyst) – Solvent free
DAP	Inorganic	Diammonium hydrogen phosphate aqueous solution (+ $CaCl_2$ and EtOH)
PEG	Modified alkoxysilane (Hybrid)	Tetraethoxysilane(TEOS)-based solution containing polyethylene glycol (acid catalysed) – Solvent: EtOH
HAp	Alkoxysilane with nanoparticles	TEOS-based solution containing comercial SiO2 nanoparticles (acid catalysed) – Solvent: EtOH
SiO_2	Alkoxysilane with nanoparticles	TEOS-based solution containing laboratory developed hydroxyapatite (HAP) nanoparticles (acid catalysed) – Solvent: EtOH

Five consolidant products were used to apply to each lithotype, of which four are alkoxysilane-based and one inorganic ammonium phosphate-based consolidant (referred to hereafter as DAP), more information about the consolidant products can be found in Table 2. The four alkoxysilane-based consolidants corresponded to: a commercial product (Wacker SILRES® BS OH 100, referred to hereafter as BS-OH); a hybrid consolidant (modified alkoxysilane, referred to hereafter as HCl.PEG) and two consolidants with added nanoparticles of different natures (referred to hereafter as HCl.nHAp

(Rodrigues *et al.* 2021[1]) and HCl.nSiO$_2$). The last three consolidant products were developed within the framework of the NanoCStoneH research project.

2.2.2. Treatments

The application method for the treatment of both carbonated marble varieties was brushing:

- Decayed marble: application until apparent saturation for all consolidant products and retreatment until apparent saturation (T_{sat}) on HCl.nHAp, HCl.nSiO$_2$, and HCl.PEG products (one month after the first application);
- *Pedra de Ançã* Block A2 (sound): application until apparent saturation (T_{sat}) for all products;
- *Pedra de Ançã* Block A6 (sound): application until 10mm depth (T_{10mm}) (observed in the lateral faces of the samples).

The amount of product absorbed was determined by weighing the samples before and immediately after treatment and is expressed as the weight of product per unit surface (kg/m^2), Table 3. To avoid rapid evaporation of the solvents the samples were wrapped in parafilm (for 48 hours) and conditioned in a dry chamber (at conditions of 22°C and 45% temperature and relative humidity) until their mass stabilized. Afterward, the dry residue was determined by subtracting the stabilized mass of the samples from the mass before treatment and is expressed as the weight of product per unit surface (kg/m^2), Table 3.

Table 3 – Products application to apparent saturation (marble and Block A2) and até 10mm de profundidade (Block A6).

	Product absorved $[kg/m^2]$				**Dry residue** $[kg/m^2]$		
	Marble		**Block A2**	**Block A6**	**Marble**	**Block A2**	**Block A6**
	1st	**2nd**			**Total**		
BS-OH	0,19±0,03	-	6,47±0,84	2,11±0,13	0,07±0,01	2,60±0,32	0,82±0,04
HCl.nHAp	0,21±0,06	0,13±0,02	6,36±0,64	2,02±0,15	0,05±0,01	1,14±0,12	0,32±0,01
HCl.nSiO$_2$	0,20±0,04	0,11±0,02	6,07±0,29	2,29±0,32	0,04±0,01	1,08±0,07	0,35±0,06
HCl.PEG	0,22±0,05	0,10±0,02	5,70±0,50	2,23±0,16	0,05±0,03	1,57±0,15	0,53±0,07
DAP	0,19±0,03	-	8,30±0,72	2,29±0,20	0,01±0,01	0,36±0,07	0,09±0,01

1st – First application to apparent saturation; 2nd – Second application to apparent saturation (retreatment).

The marble samples treated (T_{sat}) with the various consolidants generated very equivalent amounts of absorbed product and the standard deviations are related to the heterogeneity of the samples and the reduced amount of absorbed product in absolute terms, which implies a lower accuracy. In the second application of the consolidants (HCl.nHAp, HCl.nSiO$_2$, and HCl.PEG), the values of absorbed product are equivalent for the various consolidants.

The consolidation treatments on Block A2 (T_{sat}) and Block A6 (T_{10mm}) caused similar absorbed products for the various consolidants, of approximately 6.0 kg/m2 and 2.0 kg/m^2, respectively. The absorbed product of samples from Block A6 is 3 times lower than that of samples from Block A2.

In the marble and *Pedra de Ançã* samples the BS-OH product stands out because it presents a higher dry residue associated with the absence of solvent and the DAP product is the one that presents the lowest dry residue. In the case of marble samples, the two applications of HCl.nHAp and HCl.nSiO$_2$

consolidants were not enough to generate quantities of dry residue equivalent to the BS-OH product, with only one application in the porous structure of the marble.

2.2.3. Methodology to assess incompatibility risks

The methodology used was proposed by Delgado Rodrigues and Grossi (2007) and contemplates several criteria that are subdivided into a set of compatibility indicators to which a scale of incompatibility risk is associated, Table 4. Sena da Fonseca (2018) for the study of porous limestones added other indicators, which are hardened surface crust (drilling resistance: the ratio between surface resistance and deepness) and dry residue, for the application of the methodology.

Table 4 – Incompatibility risks (adapted from Delgado Rodrigues & Grossi, 2007)

Criteria	Compatibility indicator		Incompatibility risks (rating scale – C_n))
Visual properties	Total colour difference (ΔE*)	ΔE* < 3 3 < ΔE* < 5 ΔE* > 5	0 5 10
Mechanical properties	Hard crust*	Value < 10% 10% < Value < 25% Value > 25%	0 5 10
Treating ability	Penetration depth	h > 20 mm 5 < h < 20 mm h < 5 mm	0 5 10
Hidrophilic behaviour	Water absorption coefficient Drying index Water vapour permeability	Value < 10% 10% < Value < 25% Value > 25%	0 5 10
Physical disturbance	Dry residue*	Value < 1 kg/m^2 1 kg/m^2 < Value < 2 kg/m^2 2 kg/m^2 > Value	0 5 10

(*) – indicators added from Sena da Fonseca (2018).

Using the rating scale in Table 4 and the following mathematical equation, it is possible to determine the degree of incompatibility of a given consolidation treatment:

$$ID_n = \sqrt{\frac{C_1^2 + C_2^2 + \cdots + C_n^2}{n}} \qquad \text{(Equation 1)}$$

Where:

ID_n – incompatibilty degree;

$C_1 \dots C_n$ – Incompatibility risk;

n – number of indicators used to calculate ID.

To determine the compatibility indicators, the following tests were performed on untreated (reference) and treated samples Determination of water absorption coefficient; Determination of drying index; Determination of water vapour permeability; Colorimetric characterization. For the *Pedra de Ançã*, the dry residue and the hardened surface crust were added to the listed compatibility indicators, whose data were obtained from Sena da Fonseca et al. 2021.

3. Results

3.1. Alterations promoted by the treatments

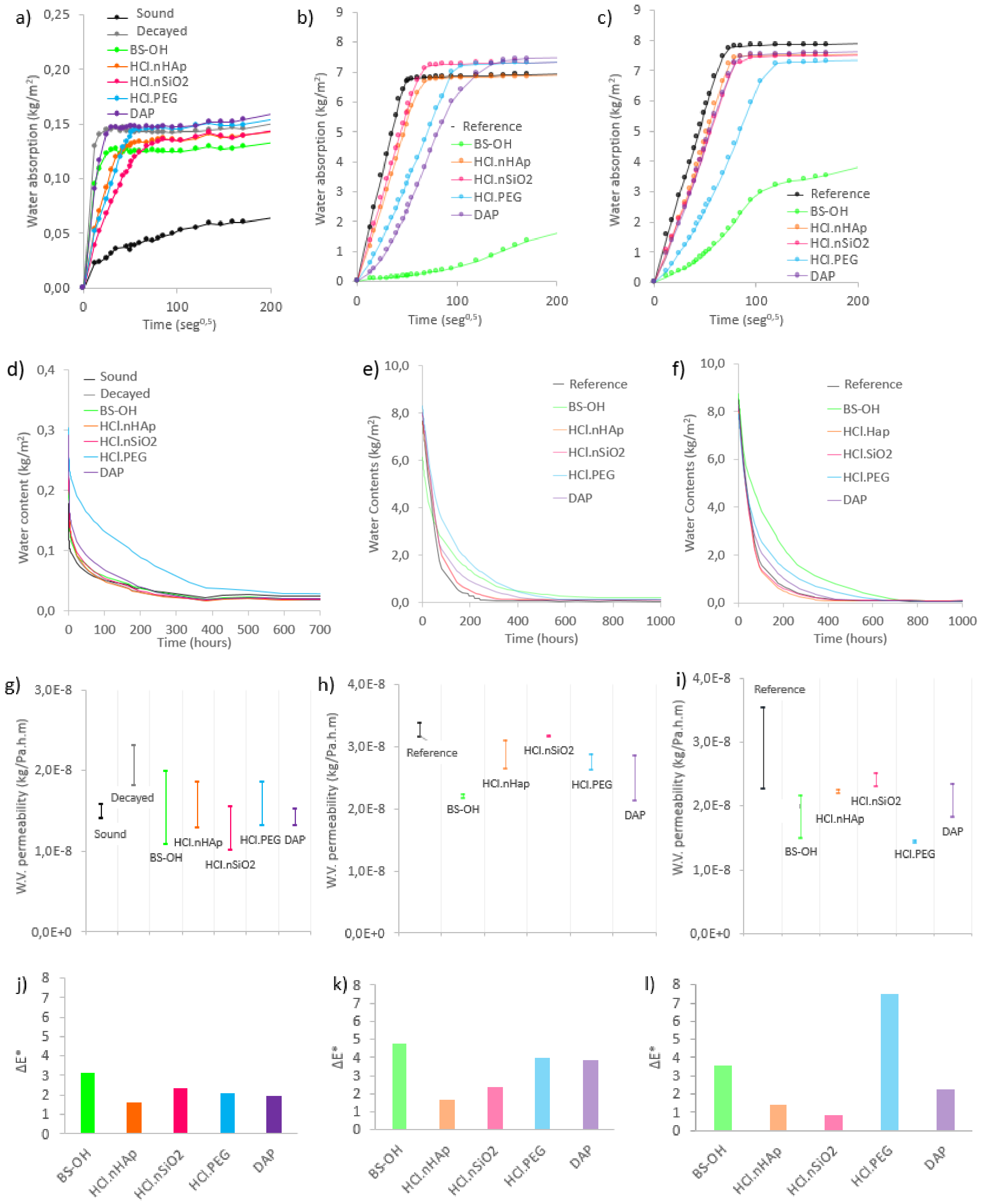

Figure 1 – Water absorvation by capilarity: Marble (a), Block A2 (b) and Block A6 (c); water evaporation kinetics: Marble (d), Block A2 (e) and Block A6 (f); water vapour permeability: Marble (g), Block A2 (h) and Block A6 (i); Total colour difference: Marble (j), Block A2 (k) and Block A6 (l).

Figure 1 shows the water transport properties of the untreated samples (reference) and of the treated samples, as well as the color change that the consolidation treatment caused.

For the marble samples, the behavior of the water absorption curves by capillarity, Figure 1 (a), of the generalized degraded treated samples remained closer to the samples in a degraded state than to those considered to be in a sound state, and far from restoring the properties.

The treatments on the degraded marble samples led to a slight reduction of the net conductivity in the drying curves, Figure 1 (d), however, this change was not sufficient to restore the properties of the untreated healthy samples. The HCl.PEG product showed the most significant change in drying kinetics properties.

In water vapor permeability, Figure 1 (g), the treatments allowed the treated samples to restore the water vapor permeability characteristics of the marble in its sound state. Concerning the aesthetic changes, Figure 1 (j), the treated degraded samples turned slightly more yellow than the untreated ones.

In *Pedra de Ançã*, the kinetics of water absorption in samples treated until apparent saturation, Figure 1 (b), and up to 10mm depth, Figure 1 (c), with the consolidant products showed little significant changes when compared to untreated samples, except for BS-OH.

The drying kinetics in the treated samples of *Pedra de Ançã* was more influenced for the samples until apparent saturation, Figure 1 (e), than up to 10mm depth, Figure 1 (f), being the behavior of the products HCl.nHAp and HCl.nSiO_2 closer to the untreated samples.

The coefficient of permeability to water value suffered a generalized reduction for all treated samples until saturation, Figure 1 (h), and up to 10mm depth, Figure 1 (i), in relation to the untreated samples.

In *Pedra de Ançã*, the treatments led the treated samples to be darker and more yellow than the untreated samples, and the color change was greater for the application up to 10mm depth, Figure 1 (l), than the application up to apparent saturation, Figure 1 (k).

3.2. Compatibility assessment

With the characterizations of the untreated and treated samples presented in the previous chapters and with the DRMS data of Sena da Fonseca el al. (2021), each of the compatibility indicators were classified in relation to the risk of incompatibility and the respective degree of incompatibility was determined, for the products applied until saturation in the marble, Table 5, and in the *Pedra de Ançã* and for the products applied until 10mm depth, Table 6.

In both situations, the compatibility indicators are expressed through the percentage of the variation of the values of the characteristics evaluated in untreated and treated samples compared to the respective values obtained in untreated samples.

The consolidant products were applied to degraded marble samples, so the study of potential compatibility was carried out in relation to untreated degraded marble samples and in relation to treated sound marble samples, Table 5. The consolidating treatments show a significantly lower degree of incompatibility when this took as reference the characteristics of the non-degraded healthy marble.

In situations where the entire degraded thickness is consolidated, for which the use as reference of the properties in the sound state is the most correct way to evaluate the incompatibility potential of a given consolidating treatment, the performed treatments showed low incompatibility potential (ID between 0 and 5).

Table 5 – Treatments applied to degraded marble - Incompatibility risk (C_n) and Incompatibilty degree (ID).

Compatibility indicator	**BS-OH**	**HCl.nHAp**	**HCl.nSiO2**	**HCl.PEG**	**DAP**	**BS-OH**	**HCl.nHAp**	**HCl.nSiO2**	**HCl.PEG**	**DAP**
	Ref.: Marble decayed untreated samples					**Ref.: Marble sound untreated samples**				
Penetration depth (mm)	0	0	0	5	0	0	0	0	5	0
Water absorption coefficient (%)	5	10	10	10	0	0	0	0	0	10
Drying índex (%)	0	0	5	10	0	0	0	0	10	0
Water vapour permeability (%)	5	10	5	5	0	0	5	0	0	0
Total colour difference	5	0	0	5	0	5	0	0	0	0
Incompatibilty degree (ID)	4,5	6,3	5,5	7,4	6,7	2,2	2,2	0,0	5,0	0,0

*Positive percentage values mean that the characteristics of the treated samples have lower values than those of the untreated samples.

In this case, using non-degraded healthy marble samples as reference, HCl.nSiO_2 and DAP were the products that revealed the highest compatibility with marble, while BS-OH and HCl.nHAp revealed low incompatibility risk with the lithological variety studied and for the universe of properties considered.

The results obtained from the comparison of the degree of incompatibility of the application up to the apparent saturation and with the application up to 10mm deep in samples of *Pedra de Ançã*, although not very significantly, indicate that the consolidant products originate treatments that tend to have a lower degree of incompatibility when applied up to the apparent saturation than when used in applications up to 10mm deep, with the exception of the product HCl.nSiO_2. This difference is due to the fact that all products have satisfactory penetration capabilities, which contributed positively to a higher potential for compatibility in the case of treatment up to apparent saturation (this indicator was not used for brush treatment up to 10mm).

In any case, the degree of incompatibility of the *Pedra de Ançã* treated with the different consolidant products is within the same order of magnitude for both application methods, with the exception of the product HCl.nHAp and the product HCl.nSiO_2, whose type of treatment proved to be determinant for their potential compatibility.

Table 6 – Treatments applied to sound *Pedra de Ançã* - Incompatibility risk (C_n) and Incompatibilty degree (ID).

Compatibility indicator	**BS-OH**		**HCl.nHAp**		**HCl.nSiO2**		**HCl.PEG**		**DAP**	
	Apparent saturation	**10 mm deep**	**Apparent saturation**	**10 mm deep**	**Apparent saturation**	**10 mm deep**	**Apparent saturation**	**10 mm deep**	**Apparent saturation**	**10 mm deep**
Penetration depth (mm)	26	U	28	U	19	U	19	U	30	U
Dry residue (kg/m2)	2,6	0,3	1,1	0,3	1,1	0,4	1,6	0,5	0,4	0,1
Water absorption coefficient (%)	97	96	27	19	20	23	57	60	73	23
Drying index (%) (*)	-28	-70	-20	5	-15	5	-37	-28	-16	-11
Water vapour permeability (%)	32	39	12	26	2	20	15	52	23	30
Total colour difference	4,8	3,6	1,7	1,4	2,3	0,8	4,0	7,5	3,8	2,2
Hard crust* (%)	11	**	**	**	**	**	13	21	19	14

*Positive percentage values mean that the characteristics of the treated samples have lower values than those of the untreated samples. ** - Gradual decrease in depth resistance; U- Unvalued.

In global terms, the treatments with the product BS-OH were those showing the highest degree of incompatibility followed by the treatments with the product HCl.PEG., while the treatments with the product HCl.nSiO_2 were those showing the lowest degree of incompatibility among all the products studied.

Marble samples and the *Pedra de Ançã* samples from block A2 the consolidant products were applied by brushing until apparent saturation, so it is possible to make a comparative analysis of the potential incompatibility of the studied products when applied to these two stone varieties. The risk of incompatibility values for the comparison between the stone materials was obtained by taking untreated sound stone as a reference.

The analysis of the risk of incompatibility, evidently, a higher risk of incompatibility when applied to *Pedra de Ançã* than to marble, reinforcing the risks and difficulties that have been reported in consolidating very porous limestones (Delgado Rodrigues & Ferreira Pinto, 2019).

In the set of treatments studied, the products HCl.nSiO_2 and DAP were those that showed greater sensitivity to the differences in the characteristics of the supports, since they did not reveal any risk of incompatibility when applied to the marble and this risk was of the order of 4 and 5, respectively, in the *Pedra de Ançã*.

It should also be noted that the risk of incompatibility associated with the application of the BS-OH product on the *Pedra de Ançã* was particularly higher than that obtained in the marble, having been the treatment studied with the highest risk of incompatibility when applied to the *Pedra de Ançã*. This behavior also points to the fact that the potential compatibility of this product is very much conditioned by the characteristics of the supports and to a potentially higher risk of its use in porous limestones.

Of all the treatments in question, HCl.PEG was the one that revealed the greatest risk of incompatibility when applied to both varieties studied and differed negatively from the others when applied to marble.

Given the results obtained, and considering the characteristics analyzed, the products HCl.nSiO_2 and DAP were those that revealed the least risk of incompatibility for marble, and all of them manifested a significant risk of incompatibility when applied to the *Pedra de Ançã*, particularly BS-OH and HCl.PEG.

4. Conclusions

The characterization of the stone varieties showed the differences between the physical and colorimetric characteristics of the Trigache marble and the *Pedra de Ançã* (porous limestone). The differences in the pore space characteristics of the studied stones were significantly reflected in the values of porosity, the kinetics of water absorption and drying that manifested not only when sound, but also when we proceeded to the comparative analysis of the sound *Pedra de Ançã* (≈26-31%) and the artificially degraded Trigache marble (≈1%). As a consequence, the *Pedra de Ançã*, due to its high porosity and absorption capacity, presents a significantly higher capacity to absorb consolidation products compared to marble.

The consolidating products applied until apparent saturation in the degraded marble and in the sound *Pedra de Ançã*, revealed a lower risk of incompatibility for the consolidation treatments in marble, showing a higher potential for its use, both of those resulting from products based on alkoxysilanes and the inorganic product. The products HCl.nSiO_2 and DAP stood out for the lower risk of incompatibility with marble and the products BS-OH and HCl.PEG stood out for the higher risk of incompatibility for *Pedra de Ançã*.

The application of consolidating products by application up to the apparent saturation and up to the depth of 10mm in *Pedra de Ançã*, although not very significantly, revealed a tendentially lower risk of incompatibility in the treatments applied up to the apparent saturation, with the exception of the product HCl.nSiO_2. For both application methods studied in *Pedra de Ançã*, the treatments with the product BS-OH were those that revealed the highest risk of incompatibility followed by the treatments with the product HCl.PEG, while the treatments with the product HCl.nSiO_2 were those that showed the lowest risk of incompatibility.

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