TÉCNICO LISBOA

Water-repellent and consolidation stone treatments

Behaviour under a marine natural exposure condition

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Master Thesis in Civil Engineering

Extended abstract

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1. Introduction

The interest in heritage conservation has been increasing and the research on conservation treatments is gaining more and more importance. Stone degradation results from an interaction between intrinsic factors, including mineralogy, texture, porosity, etc., and extrinsic factors such as climate, the building itself (orientation of the face, surface finish, salts), physical, chemical or biological.

The principal aim of conservation action is to increase the lifetime of an object so that it remains useable in a present and future time, trying to reduce the intensity of existing degradation processes and avoiding the development of new ones. Cleaning, protection and consolidation are examples of conservation actions that are frequently performed on stone conservation interventions. In some situations, the protection of stone objects against the presence of water is achieved through the application of water-repellent products with the objective of reducing the penetration of water without blocking the pores. The water-repellent treatments should reduce the hydrophilic characteristics and the wetting ability of surfaces and capillaries. Consolidation treatments are applied when it is necessary to increase the cohesive characteristics of the constituents of stone materials. After a consolidating action, the stone must show greater cohesion, greater strength and greater resistance to environmental stresses. These treatments should also act in depth and increase the surface cohesion.

This paper presents and discusses the behaviour of water-repellent and consolidation treatments applied on five carbonate Portuguese stones exposed after 49 months in a marine environment. The initial performance of the treatments and the results obtained after 16 months of exposure can be found elsewhere (1) and will be considered on the analysis here presented.

2. Materials and methods

2.1. Stones

Ançã limestone is a homogeneous white and fine-grained stone mainly formed by calcite with high porosity that presents both low mechanical resistance and low superficial hardness. Coimbra stone is a heterogeneous yellowish stone mainly formed by dolomite that presents some softer and more porous zones (Z1) than others (Z2) that show higher hardness and lower porosity. Miocene stone is a yellowish carbonate stone mainly composed by dolomite that presents some vacuoles of different dimensions and forms. Boiça stone is a homogeneous white/grey compact carbonate stone with some calcite veinlets with a thickness lower than 0.5 mm. Lioz stone is a grey and very compact stone with very low porosity and almost formed by calcite, (1) (2) (3).

Table 1 presents some physical properties of the tested stones determined by Ferreira Pinto (1) according the Recommendations RILEM 25 PEM (RILEM 1980).

Table 1 – Stone physical properties (1)

Stone	Open porosity (%)	Real density (kg.m-3)	Bulk density (kg.m-3)
Ançã	27.2 (±1.1)	2711 (±3)	1972 (±29)
Coimbra	17.8 (±3.3)	2710 (±5)	2449 (±27)
Miocene	15.4 (±1.7)	2709 (±9)	2685 (±9)
Boiça	9.6 (±1.1)	2853 (±44)	2344 (±101)
Lioz	0.9(±0.2)	2846 (±17)	2408 (±46)

2.2. Products

Two water-repellents and three consolidation products were tested and their characterization can be found in the doctoral thesis of Ferreira Pinto (1) performed at LNEC. All the products were applied on stones slabs with a surface area of 160-280 cm^2 and a thickness of 2.5 cm (specimens type I). The water repellent products were also applied on square prisms samples with 5 cm side and 2.5cm thickness (specimens type II).

A modified siloxane (Tegosivin HL100 from Goldschimidt AG) applied in a solution of white-spirit with a proportion of 1:11 by volume (H) and a “ready to use” product (N) based on a monomeric alkylalkoxysilane in ethanol (Dynasylan NH 40 S from Hüls) were the water-repellent products tested on all the stones.

The three consolidation products applied on all the stones with exception of Lioz stone were the following: ethyl silicate, acrylic resin and epoxy resin. The tested ethyl silicate (TG) is a ready-to-use product that contains pre-polymerised TEOS in white spirit and is manufactured by Goldschmidt. The acrylic resin used was Paraloid B72, which is an ethyl-methacrylate copolymer manufactured by Röhm and Haas. Paraloid B72 was applied with the following formulation: 0.06:0.61:0.09:0.2 = resin (solid form): toluene: xylene: acetone and it will be referenced here with the acronym B. The epoxy resin tested was the EP 2101 produced by EUROSTAC. EP 2101 is a cycloaliphatic epoxy resin in the form of a 25% solution in toluene and isopropanol. The hardener is an aliphatic polyamine solution mixed with the resin to provide a consolidating system in a proportion of 1:5 (hardener: resin). In order to reduce its strengthening action, EP 2101 was diluted according to the manufacturer’s instructions by using a mixture of toluene and xylene as a solvent (in a proportion of 1:1) to reach the final proportion of 1:1 for the consolidant: solvent mixture. This product is referenced here with the acronym EP.

All products were applied by brushing following procedures which can be consulted elsewhere (1).

2.3. Natural exposure environment and monitoring time intervals

The specimens were exposed for 49 months to the “Cabo da Roca” environment, which is a promontory in the Portuguese Atlantic west coast located 50 km west of Lisbon. It has an altitude of 140m. The specimens were mounted on a steel structure, positioned 45º to the horizontal and facing west in order to enhance the exposure to the sea spray (4).

2.4. Experimental methods

After 4 years of exposure, the surfaces of all specimens were observed visually and by resorting to a binocular loupe in order to assess their evolution and to carry out, whenever possible, a comparative analysis of the condition of the treated and untreated areas of each specimen. After this, the behaviour in time of the tested water-repellent and consolidation treatments were evaluated by the determinations presented in Table 2. The tested specimens were monitored after 16 months and 49 months of exposure. For simplification purpose, the monitoring steps will be referred as being done after the first and fourth year of exposure. The initial characterisation of the treatments and after the first control was published elsewhere and both were used for assessing the evolution of the treatments over time, (1), (4).

Table 2– Determinations used for the assessment the behaviour in time of the treatments

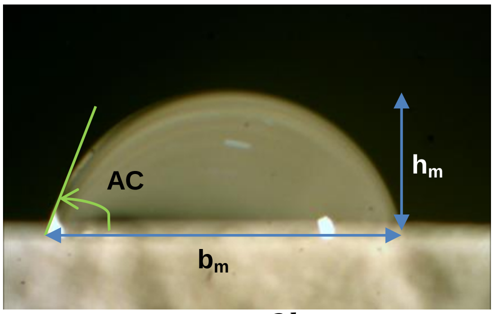
Determination	Type of treatment		
	Water- repellent		Consolidation
	Type I	Type II	Type I
Micro-drops absorption time	X	X	X
Contact angle		X	X
Water absorption (pipe method)	X		X
Colour	X		X
Superficial hardness			X
Drilling resistance			X

The micro-drops absorption time is the ratio (MD - expressed as a percentage) between the evaporation/absorption time (tm_i) of a certain number of micro-drops (n) placed in the tested surface and a similar number of micro-drops placed on a rough glass surface (t_v), (equation 1). The use of the glass surface makes it possible to compare values obtained on different occasions with different hygrometric and temperature conditions.

$$\mathbf{MD} = \frac{\sum_{i=0}^{n}\left(\frac{tm_i}{t_v}\right)}{n} \times \mathbf{100}\ [\%] \qquad \textbf{(Equation 1)}$$

The contact-angle was measured based on the procedures defined in RILEM 58 VTP recommendations under a microscope with a micro-drop of 4µl, Figure 1.

The water absorption was evaluated by the pipe method following the procedures in the RILEM 25 PEM, Figure 2, and it was determined the amount of water absorbed at the end of 1 hour.



$$CA = 2arc\tan\frac{2h_m}{b_m} \qquad [º]$$

Figure 1 – Contact- angle

Figure 2- Karsten Pipe method

The evolution of the colour variations promoted by the treatments was evaluated in a quantitative way by using the CIELAB system. The equipment used was a portable model X-Rite with a circular measuring window with a diameter of 2cm (area of 3.14cm^2) and automatic data acquisition. The colour quantification was obtained by using the coordinates in the chromatic colour palette of reference CIE 1931, in the uniform CIE 1976 (L* a* b*) colour space or CIELAB. Colour measurements were evaluated with CIE 10 degree standard observer (1964) and CIE standard illuminant D65. The basic coordinates L*, a*, b* of the system CIELAB and chroma were used. L* may vary between 0 (black) and 100 (white), a* is positive in the red direction and negative in the green direction, and b* is positive in the yellow direction and negative in the blue direction. The value of chroma, i.e., the colour saturation, C*, is obtained by using the equation 2. The colour modifications induced by the consolidation treatments and their evolution due to the exposure are represented as the differences of L*, a*, b*, and C* between the values measured after treatment, or after exposure, and before treatment. ΔE* values (equation 3) represent the difference in total colour between the treated and untreated stone and are useful for a rapid evaluation of the colour changes. The larger the value of ΔE*, the higher is the colour change.

$$\boldsymbol{C^*} = \sqrt{\boldsymbol{a^{*2}} + \boldsymbol{b^{*2}}} \qquad \boldsymbol{\Delta E^*} = \sqrt{\boldsymbol{\Delta a^{*2}} + \boldsymbol{\Delta b^{*2}} + \boldsymbol{\Delta L^{*2}}}$$ **(Equation 2 and 3)**

The surface hardness was assessed with a Martens sclerometer based on the recommendation RILEM IV.1. This test is useful for evaluating the stone's mechanical properties as the hardness measured is the result of the internal cohesion and the stiffness of stone constituents. The steel tip was placed in contact with the specimen ensuring that it stays perpendicular to the surface under testing. Then a force of 3Kgf was applied on the tip and the handcart was pulled with a constant velocity until a scratch was done with a desired length. The width of each scratch (WS) was measured every 3 mm with the help of a portable magnifying glass with a light source and a micrometer (resolution of 0.02 mm).

Drilling resistance measurements were carried out with a common hard steel drill bit (Fisher type) with 5mm diameter using a Drilling Force Measurement System (DFMS). For the present study, the following drilling conditions of rotation speed and advancing rate were used: 400rpm (rotation speed) and 15mm/min (advancing rate). All the tests performed on each stone type used the same drill bit to reduce the eventual variability of the results (5) (6).

3. Results

3.1. Water repellent treatments

Table 3 presents the values of the microdrop absortion time and contact angle determined after treatment, and after 1 and 4 years of exposure. Figure 3 and Table 4 presents the values of the water absorption under low pressure obtained using the pipe method, and Table 5 presents the values of total colour variation and croma variation after treatment, and after 1 and 4 years of exposure, considering the not treated surfaces as reference.

The data obtained by Ferreira Pinto (1) with the micro-drops absorption time and contact angle after 1 year of exposure, revealed a generalized increase in the wettability of the surfaces treated with both water repellent products, where only the Ançã specimens reveal to be stable when treated with the polysiloxane (H) and still to have some effectiveness when the silane (N) is concerned. On the other hand, Ferreira Pinto also concluded (1) that the water repellent treatments still conserve a relevant capacity to reduce the water absorption of the tested stones protection although their superficial water repellence has almost completely disappeared after 1 year of exposure. Concerning the evolution of colour alterations due to the treatments, Ferreira Pinto (1) showed that they were greatly attenuated, with exception of Ançã treated with H, Table 5.

Table 3 – Water-repellent treatments – Before and after exposure

Stone and specimen type		Product H						Product N					
		MD - Microdrop absorption time [%]			CA - Contact angle [°]			MD - Microdrop absorption time [%]			CA - Contact angle [°]		
		MD^0	MD^1	MD^2	CA^0	CA^1	CA^2	MD^0	MD^1	MD^2	CA^0	CA^1	CA^2
Ançã	**I**	79	139	96				165	50	69			
	II	122	119	115	105	99	93	146	59	67	135	88	93
	II	138	130	118	109	111	99	129	79	63	131	99	84
Coimbra	**I**	112	98	100				154	60	44			
	II	104	57	n.d.	114	48	n.d.	159	6	n.d.	131	23	n.d.
	II	110	77	93	104	70	84	161	31	63	131	47	68
Miocene	**I**	106	26	80				131	99	26			
	II	83	78	68	98	67	60	110	45	14	120	42	21
	II	116	64	57	103	55	52	122	46	8	117	50	17
Lioz	**I**	51	52	55				122	49	n.d.			
	II	131	58	47	86	61	66	155	64	34	104	59	51
	II	114	56	59	78	47	57	71	67	37	102	59	51

- [0] after treatment, (1); [1] – after 1 year of exposure, (1); [2] – after 4 years of exposure; n.d. - not determined

After 4 years of exposure, the visual appearance of the treated and not treated surfaces of the exposed specimens provided relevant information about the behaviour of the treatments. The areas of the Ançã and Coimbra stone specimens not treated become eroded at the end of the exposure and similar to those treated with product N. The areas of Ançã stone treated with N were the most degraded. The surfaces of Ançã and Coimbra stone treated with product H were in quite good conditions after 4 years of exposure. The surfaces of the Miocene and Lioz stone specimens treated and not treated with both water-repellents were visually similar presenting some erosion signs. A more detailed observation of the Miocene and Lioz stone specimens surfaces showed lower erosion on the treated surfaces and a better behaviour of the treatments performed with product H.

Table 4 - Water absorption after 1 hour (pipe method), non-treated stones

Stone	Water Absorption by pipe method after 1h[cm^3]
Ançã	Higher than 4
Coimbra	0.775
Miocene	0.475

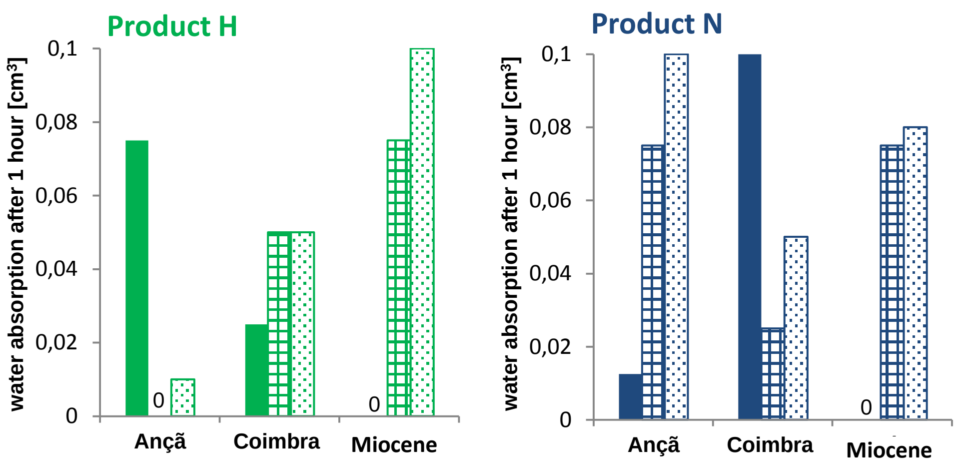


Figure 3 - Water-repellent treatments – Water absorption after 1 hour (pipe method), before and after exposure

The data obtained after 4 years of exposure points out that the main alterations registered based on the tested properties of the treatments occurred during the first year of exposure, although relevant alterations on the state of conservation of surfaces of some specimens occurred between the 1st and 4th year of exposure. In Figure 4 is possible to observe the erosion present on the not treated and treated areas of the Ançã and Coimbra stone specimens treated with product N. The development of the superficial erosion occurred between the 1st and 4th year of exposure.

Both water repellents have shown to be significantly affected by exposure, and the large majority of the surfaces of the specimens have shown a clear loss of water repellence after 1 year of exposure, Table 2. Similar situation was identified for the water absorption reduction, which registered the main alterations during the 1st year of exposure and remained more less stable, or increased slightly, between the 1st and 4th year of exposure, Figure 3. The evolution of colour variation also points out that they were attenuated during the 1st year for majority of the treatments and no relevant evolution was registered between the 1st and 4th year of exposure, Table 5.

Table 5 - Water repellent treatments – Total colour variation and croma variation evolution over time

Stone-product	ΔE^{*0}	ΔE^{*1}	ΔE^{*2}	ΔC^{*0}	ΔC^{*1}	ΔC^{*2}
Ançã - H	5.13	7.60	1.47	3.44	5.67	1.23
Ançã - N	3.12	1.50	1.47	2.26	-0.11	1.25
Miocene - H	6.22	1.80	3.25	3.95	-0.48	-1.09
Miocene - N	3.42	1.80	1.54	2.86	1.60	1.39
Coimbra - H	3.64	1.20	2.73	1.43	0.38	1.33
Coimbra - N	3.39	1.00	3.41	2.15	-0.36	3.20
Lioz - H	6.83	1.80	4.62	3.22	1.44	2.85
Lioz - N	2.51	1.10	n.d.	1.12	0.38	n.d.

- [0] after treatment, (Ferreira Pinto, 2002); [1] – after 1 year of exposure,(Ferreira Pinto, 2002); [2] – after 4 years of exposure; n.d. – not determined

The performance of the treatments after exposure reveals that the silane product (N) is less durable than the polysiloxane (H) and can be responsible for reduction the intrinsic durability of the stones, mainly if they are more porous like the Ançã and Coimbra stones.

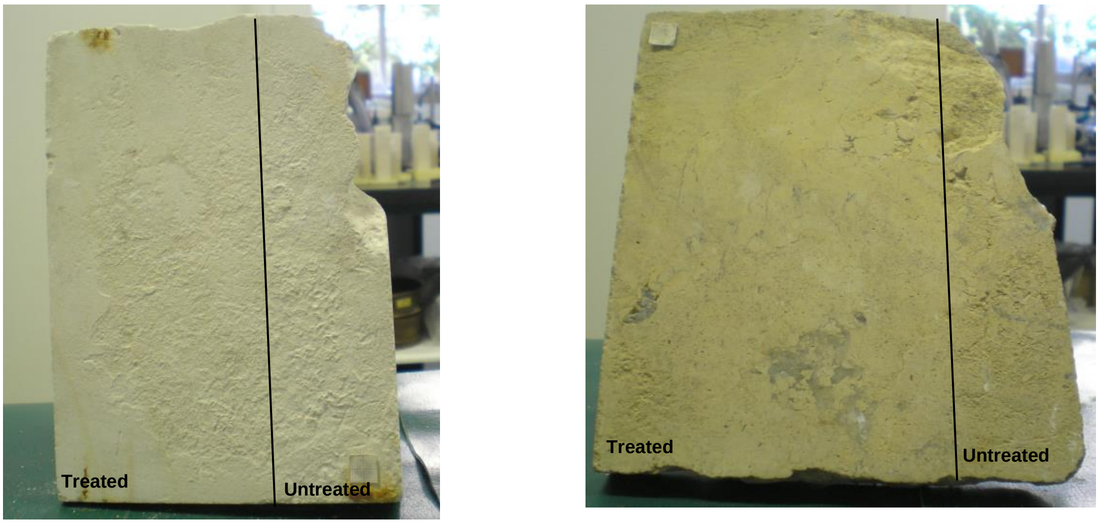


Figure 4 – Ançã (left) and Coimbra (right) specimens treated with product N after 4 years of exposure

3.2. Consolidation treatments

Figure 6 and Table 6 present the values of the superficial hardness and the drilling resistance of the treated and untreated areas of the exposed spevimens, respectively. Table 7 and Figure 7 present the evolution of the values of the microdrop absorptin time and water absorption under low pessure after 1 hour. Table 6 presents the values of total colour variation and croma variation after treatment, and after 1 and 4 years of exposure, considering the not treated surfaces as reference.

Ferreira Pinto (1) reported that, after 1 year of exposure, all specimens registered surface degradation both in untreated and treated areas identified by the reduction of the superficial hardness, with exception of the B and EP treatments on Ançã stone that revealed an increment of their superficial hardness. It was also reported other alterations on all tested consolidation treatments such as the reduction of the color variation iniattially promoted by the treatments and the increase of the water absorption, while the resistance in depth remained relatively unchanged.

After 4 years of exposure, the visual appearance of the specimens shows that for some stones the degradation of their surfaces was more notorious or similar on treated areas than in non-treated. This behaviour was identified on the: Ançã stone treated with TG, softer areas of Coimbra stone (Z1) treated with B and EP products, hardener areas of Coimbra stone (Z2) treated with EP, Miocene treated with EP and Boiça treated with B, Figure 5.

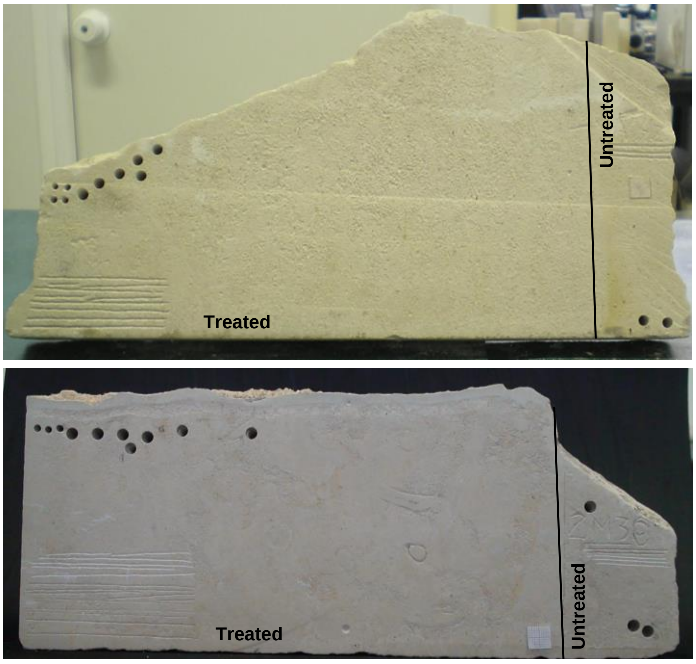
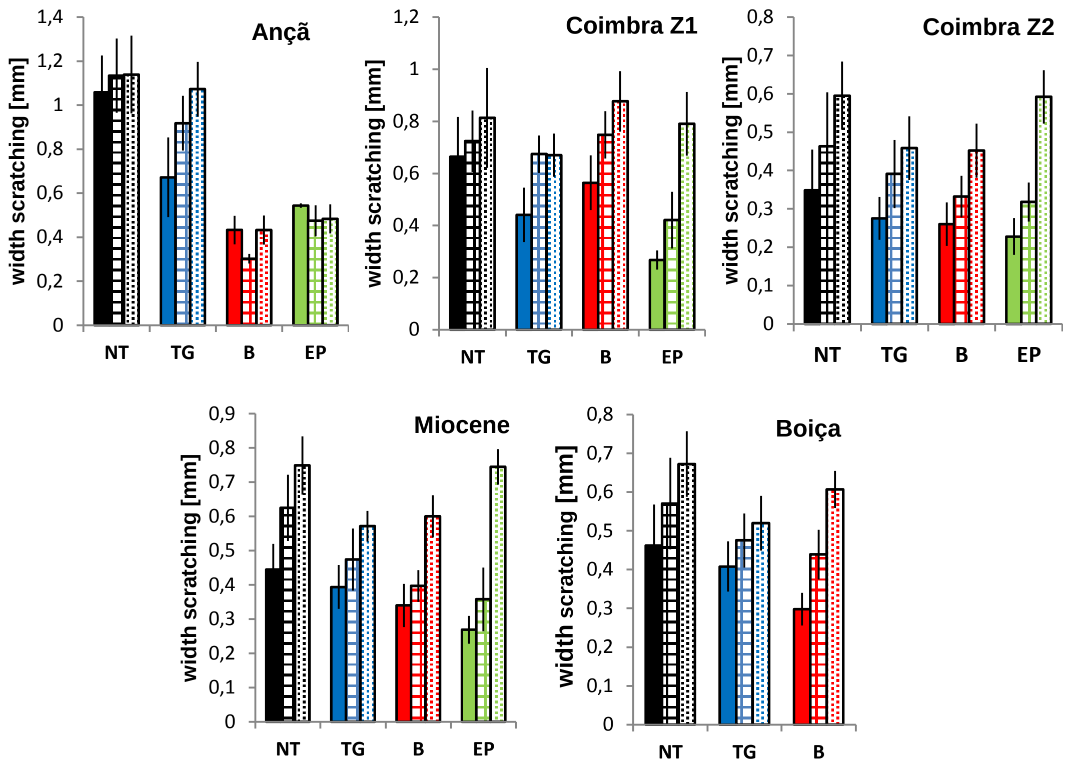


Figure 5 – Ançã (up) treated with product TG and Miocene (down) treated with product EP after 4 years of exposure

The results after 4 years of exposure show a higher rate of surface hardness reduction during the 1st year of exposure than between the 1st and 4th year, with exception of the treatments performed on Coimbra, Miocene with products B and EP and Boiça stones with product B that revealed an important reduction of their superficial hardness during the last period of exposure, Figure 6.



● the values are average values (±standard deviation)

● NT – not treated;; full bars - after treatment ; "square" bars - after 1 year of exposure; "points" bars - after 4 years of exposure

Figure 6 - Superficial hardness of untreated and treated specimens before and after 1 and 4 years of exposure

Although the resistance in depth remained relatively unchanged during the 1st year of exposure, during the following period the results of the drilling resistance points out that a process of reduction of this resistance has been started on all Boiça stone treated with TG and B, all the stones treated with the EP products, and on Ançã and Miocene stone treated with B, Table 6.

Table 6 - Driling resistence of untreated and treated specimens, before and after 1 and 4 years of exposure

	Product	**FM^0 [N]**	**depth [mm]**	**FM^1 [N]**	**depth [mm]**	**FM^2 [N]**	**depth [mm]**
Ançã	**NT**	2.6	2-18	-	-	2.7	2-18
	TG	4.4	0-20	4.4	0-20	4.3	0-20
	B	19.3	0-5	23.1	0-6	19.7	0-5
	EP	19.1	0-10	21.2	0-12	20.9	0-12
Coimbra Z1	**NT**	10	2-18	-	-	7.2	2-18
	TG	12.4	0-2.5	12.1	0-2.5	11.1	0-2.5
	B	9.6	0-2	7.8	0-2	6.0	0-2
	EP	19.8	0-4	17.1	0-3	12.5	0-3
Coimbra Z2	**NT**	44.6	2-18	-	-	35.6	2-18
	TG	50.3	0-3	60.4	0-4	38.7	0-4
	B	31.8	0-3	-	-	-	-
	EP	63.8	0-4	67.4	0-4	47.3	0-4
Miocene	**NT**	21.3	2-18	-	-	20.5	2-18
	TG	22.5	0-5	24.7	0-4	21.4	0-4
	B	24.9	0-5	27.2	0-2	19.3	0-2
	EP	26	0-3	24.2	0-3	16.1	0-3
Boiça	**NT**	16.5	2-18	-	-	13.4	2-18
	TG	17	0-5	14.6	0-4	10.9	0-4
	B	21.2	0-4	18.9	0-2	15.4	0-2

- [0] after treatment, (Ferreira Pinto, 2002); [1] – after 1 year of exposure,(Ferreira Pinto, 2002); [2] – after 4 years of exposure; - – not determined

The superficial water absorption ability of the treated surfaces was strongly increased after the 1st year of exposure and remains similar after 4 years of exposure, as shown by the microdops absorption time values present in Table 7.

Table 7 - Microdrop absorption time of untreated and treated specimens, before and after 1 and 4 years of exposure

stone	Product	MD⁰ [%]	MD¹ [%]	MD² [%]
Ançã	TG	18	1	2
	B	96	8	7
	EP	9	1	1
Coimbra Z1	TG	129	6	8
	B	79	2	1
	EP	31	3	4
Coimbra Z2	TG	123	21	13
	B	112	18	14
	EP	27	6	6
Miocene	TG	98	21	10
	B	99	11	16
	EP	49	7	5
Boiça	TG	145	13	11
	B	62	5	16

- [0] after treatment, (Ferreira Pinto, 2002); [1] – after 1 year of exposure,(Ferreira Pinto, 2002); [2] – after 4 years of exposure; n.d. – not determined

The results of the water absorption (pipe method) also show that the initial reduction of the stones water absorption promoted by the treatments was significantly reduced as a consequence of the 1st year of exposure, and has not changed substantially following the next exposure period, Figure 7. The most relevant alteration registered on the water absorption of the treated specimens after the 4th year of exposure occurred on Ançã stone treated with TG.

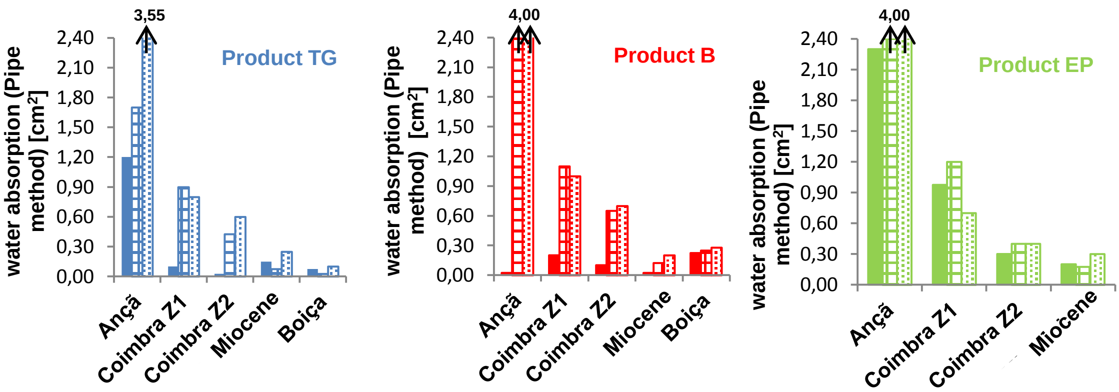


Figure 7 - Water absorption (after 1h) of untreated and treated specimens before and after 1 and 4 years of exposure

The evolution of colour variation also points out that the colour variations promoted by the tretaments were strongly attenuated during the 1st year for all the treatments and no relevant evolution was registered between the 1st and 4th year of exposure, Table 8, except for Ançã stone treated with the acrylic resin (B) that registered a very relevant increase in total colour variation.

Table 8 - Consolidation treatments – Total colour variation and croma variation evolution over time

Stone-product	ΔE*⁰	ΔE*¹	ΔE*²	ΔC*⁰	ΔC*¹	ΔC*²
Ançã - TG	5.22	0.90	1.86	2.59	-0.12	1.15
Ançã - B	8.92	5.36	11.63	5.53	3.26	8.20
Ançã - EP	13.58	4.59	5.36	8.00	0.27	2.44
Coimbra - TG	11.57	3.38	4.53	4.56	1.37	1.77
Coimbra - B	9.16	3.43	2.58	5.78	0.16	2.26
Coimbra - EP	10.32	1.42	1.92	4.13	-0.79	1.73
Miocene - TG	9.63	0.89	0.80	6.10	-0.13	-0.14
Miocene - B	7.23	0.53	3.42	5.77	-0.39	2.79
Miocene - EP	7.87	2.44	1.27	5.72	-1.18	0.88
Boiça - TG	10.12	2.37	1.95	5.43	-1.66	1.69
Boiça - B	5.00	1.51	2.93	3.78	-0.86	1.91

- [0] after treatment, (Ferreira Pinto, 2002); [1] – after 1 year of exposure,(Ferreira Pinto, 2002); [2] – after 4 years of exposure; n.d. – not determined

4. Conclusions

The methodology followed in this study, established by Ferreira Pinto (1), proved to be effective for assessing the degradation susceptibility of both type of treatments under natural exposure conditions and for discriminating their corresponding performance in time. The evolution in time revealed by both type of treatments highlighted the importance of these studies for assessing the potential performance of a treatment, the high probability of occurring relevant reduction of the performance of a treatment just after 1 year of exposure, the possibility of a treatment being responsible for reduction the stones natural durability and the influence of the stone properties on the behaviour of a treatment with a specific product. The information about the behaviour of the treatments under natural exposure conditions obtained by Ferreira Pinto (1) after only 1 year of exposure showed that this type of assessment can be particularly informative even after a short period of exposure, mainly when water-repellent is concern. The assessment of longer periods of exposure allow confirmation of some evidences that might be identified when monitoring shorter periods of exposure and the potential risk of a treatment being responsible for reducing the intrinsic durability of the stones.

Ferreira Pinto concluded that the silane product was more efficient than the polysiloxane in all tested stones and also less durable than the polysiloxane based on the behaviour of water-repellent treatments after 1 year of exposure, (1). The results here presented, obtained after 4 years of exposure, confirmed the lower durability of all tested silane treatments and highlighted the risk of having a reduction of the intrinsic durability of the stones when silane products are applied, mainly if they are more porous like the Ançã and Coimbra stones.

Concerning the behaviour of the consolidation treatments at the end of the 1st year of exposure, the characterization performed by Ferreira Pinto identified evidences of some superficial degradation on the treated surfaces, with exception of the B and EP treatments on Ançã stone, (1). The monitoring performed after 4 years of exposure showed that the consolidation treatments can be responsible for reducing the intrinsic durability of the stones, highlighted the reduction of the surface hardness of some treated surfaces previously identified and a tendency for the in-depth of the degradation.

Acknowledgements

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