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A.Elena Charola and J. Delgado Rodrigues, Editors
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Effectiveness and stability over time of water repellent treatments in carbonate and granitic stones

Ana Paula Ferreira Pinto
DECivil, ICIST, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal, anapinto@civil.ist.utl.pt

José Delgado Rodrigues
Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, delgado@lnec.pt

SUMMARY: Two carbonate stones and one granite in two alteration stages were treated with silanes and polysiloxanes to study the influence of the support, the relevance of the amount of product applied and the stability in time of the initial water repellent effect. This study shows that the support and the amount of product applied influence the initial effectiveness of the water repellent treatment and therefore both parameters have to be taken into account when evaluating water repellent products. It is also shown that about one year of natural exposure is sufficient to induce recognisable variations in the monitored parameters suggesting that this aging procedure can be taken as a feasible alternative when studying these products. The artificial aging carried out in the laboratory with T and RH plus UV radiation also induced measurable variations, thus confirming its usefulness for studying the stability of the induced water repellency over time..

KEY-WORDS: Immediate effectiveness; delayed effectiveness; treatment selection; amount of product; type of stone and product

INTRODUCTION

The performance of an applied water repellent treatment can be assessed through its effectiveness, unwanted changes or harmfulness, and durability. Therefore these properties need to be carefully evaluated and preferably in the same sequence since an ineffective treatment, no matter how durable, is useless. But an effective product can induce unwanted changes or result harmful, and therefore this property needs to be tested in the second place.

Water repellent treatments aim to reduce the penetration of water into the porous structure of materials by reducing the hydrophilic characteristics of the treated surface. By preventing the ingress of water, the deterioration processes that need its presence are mitigated and potentially controllable. The objective expected when applying a water repellent treatment, is its immediate ability to change the behaviour of the treated surface in the presence of water reducing its wettability thus limiting the penetration of water into the interior of the material. This is to be taken as a priority.

Changes in the wettability of the treated surface can be evaluated by resorting to the determination of the contact angle and the microdrops absorption time. The assessment of the changes in water absorption dynamics is also a relevant complement that considers both the surface and subsurface action of the water repellent. Past experience shows that water repellent products are not universally effective, and that their protection towards water absorption is reduced over time; moreover, it is also known that products that perform well on some stones may have unsatisfactory behaviour in others.

The influence of the substrate has been investigated in previous studies [1,2,3,4] and the results have shown that there is not a universally applicable protective treatment [3]. To ensure the efficacy of a water repellent treatment the amount of product applied must also be taken into consideration [5]. Another issue to ponder is the rapid decrease in the effectiveness of these treatments after artificial and natural weathering as previously reported [6].

The paper presents a study on the effectiveness of four commercial water repellents, two polysiloxanes (H and S) and two silanes (N and Q), applied on both carbonated and granitic Portuguese stones. The effectiveness was evaluated through the determination of microdrop absorption times, contact angle and the water absorption under low pressure by the pipe method. Both the type and amount of product applied influence the final behaviour of the treated surfaces.

It is known that the methods used to assess the treatments durability (either artificial weathering experiments in laboratory or the natural exposure tests with relatively small samples) do not reproduce reality in its total complexity since a building will have different exposures and areas prone to varying conditions, and therefore, the obtained results only represent the relative resistance of the treatments under the considered conditions. Nevertheless the information they provide is very relevant and should be integrated in the process of selection of water repellent treatments for stone conservation.

The susceptibility of some water repellent treatments under artificial weathering experiments and natural exposure are also presented to illustrate the fast loss of superficial water repellency in several of the tested stones, and how to differentiate this loss from the still effective hydrophobicity within a certain depth inside the stone.

MATERIALS AND METHODS

Tested stones

Different stone varieties used in many historic buildings in Portugal were selected for this research, two carbonated stones (a limestone and a dolostone) and a granite variety with different weathering states.

The tested limestone (A), quarried in the Ançã region, is a very homogenous, extremely fine grained, white stone with high porosity, and almost exclusively consisting of calcite.

The dolostone (D), quarried in Coimbra, is a calcitic dolostone mainly constituted of dolomite besides minor amounts of silica and alumina, possibly related to the presence of clay minerals. It is a heterogeneous brecciated stone material. It has a yellowish colour and in some cases a relevant presence of fissures filled with iron oxides and calcite can be observed.

The tested granite is a medium grained rock, having a granular texture and composed of plagioclase, alkali feldspar and quartz as principal constituents, with biotite, chlorite and apatite as accessory minerals. The specimens used for the present study were obtained from blocks extracted from a quarry near Évora with different weathering states. Slightly weathered (GB) and moderately weathered (GD) varieties were selected. Plagioclases are weathered in both states and quartz is fractured. However, in the more weathered granite samples (GD), a more widespread distribution of “dirt” spots in the plagioclase grains and a more pronounced chloritisation of biotite, as well as a more intense fissuration of quartz crystals are present [7].

Table 1 presents the main physical properties of the tested stones, determined according to Recommendations RILEM 25PEM [8].

Table 1.Physical properties of the studied stones

Stone	Porosity (%)	Real density ($kg.m^{-3}$)	Bulk density ($kg.m^{-3}$)
Limestone (A)	26-29	2710-2713	1930-2000
Dolostone (D)	13-22	2820-2860	2240-2480
Granite B (GB)	1.2	2660	2630
Granite D (GD)	2.9	2690	2610

Water repellent products and their application

Two silanes (N and Q) and two oligosiloxanes (H and S) available in the market were selected and tested. Products S and N are commercialised as “ready to use” products. Products Q and H are supplied in concentrated solutions that are to be diluted.

Product N is a “ready to use” product based on a monomeric alkylalkoxysilane in ethanol (Dynasylan NH 40 S, made by Hüls) having a solids content of 40%. Product Q (Q1-2306, made by Dow Corning) is an isobutyltrimethoxysilane and was applied diluted in ethanol at 60% by weight.

Product H is an oligosiloxane (Tegosivin HL100, from Goldschmidt AG) that contains reactive alkoxy (methoxy and ethoxy) groups attached to the silicon atoms and was applied in a solution of white-spirit with a proportion of 1:11 by volume. Product S is a short-chain siloxane oligomer (SILIKER S-101, supplied by Wacker Química Portugal).

The products were applied under laboratory conditions (18-25ºC temperature and 60-70% RH) to specimens previously dried at 60ºC and stabilized in laboratory for at least one month. The treated specimens were kept in the same environment for a period that ranged between 15 and 30 days.

Two different specimen sizes were used for the carbonate stone, a slab specimen (160x280x2.5 cm) and at least two square prisms (5x5x2 cm) per applied product were treated with products N and H. Both products were applied by brush and each treatment consisted of two applications of the product, in the same day, with a 4-hour time interval between them. This procedure was repeated 2 days later. The amount of product absorbed was determined by weighing the specimens at each step of the application procedure. The values presented in Table 2 correspond to the average of the total amount of product absorbed for each tested situation (stone-product).

At least four square prismatic specimens with 5x5x2 cm or 5x5x4 cm were treated for each combination of altered granite-product. The application of products Q and S on the granitic specimens was made by capillarity based on the procedures established in BS 6477:1984 [9]. These specimens were immersed 10mm into the product for 30 seconds and afterwards left to drip for 10 seconds. The amount of product absorbed, Table 2 (presented as weight per unit of surface treated) was calculated as the weight difference of the application container with the water repellent, determined immediately before and after the application.

In spite of the differences that exist among the treatment procedures, the results presented in Table 2 show the role that porosity has on the amount of product taken up during application, a fact that is valid for stones with very low porosity like granites.

Experimental procedures

The treatments were firstly evaluated in terms of their effectiveness, that is water repellency and water absorption reduction. For this purpose, results from the measurements of the contact angle and the microdrop absorption times were used. The contact angle was measured under microscope for a 4μl microdrop following a technique adapted from the photographic method proposed by Castro [10]. All the treated specimens were used to assess the immediate effectiveness of the tested water repellent treatments.

The microdrop absorption time is the ratio (expressed as a percentage) between the evaporation time of a given number of microdrops placed on the treated surface and the same number placed on an unpolished glass surface. The use of the glass surface makes it possible to compare values obtained in different occasions and at different hygrometric and temperature conditions [11].

The immediate and delayed reduction of water absorption was evaluated by the pipe method following the procedures established in RILEM 25PEM [8].

The susceptibility of the treatments to hydrophobicity loss over time was assessed on treated samples after an accelerated ageing test and after their exposure to 15 months in an urban environment.

The treated granitic specimens were subjected to 120 cycles of temperature and humidity, followed by 400 hours of exposure to UV radiation [12]. The temperature and humidity cycles were simulated in a climatic chamber (HERAEUS HC 4030), each cycle lasting for 6 hours. The temperature and relative humidity for each cycle changed from -5ºC to 60ºC and from 30% to 95% RH, respectively. The UV radiation was simulated in a chamber (HERAEUS SUNTEST CPS), where the specimens were kept under radiation with a wavelength range of 290-800nm, with an intensity of 550W/m^2, under less than 40ºC of black body temperature. For each treatment (stone-product) at least two square prisms, 5x5x2 cm were tested.

The carbonated treated specimens were exposed on the roof of the LNEC main building (Lisbon), near the airport and roads of intense traffic [6]. The specimens were mounted on a painted galvanised steel structure, positioned at a 45º angle. They faced south, for better exposure to sun and pollution sources. The lowest row of the test rig is 0.75m above the level where it stands. For each treatment (stone-product) the following specimens were exposed: a slab specimen with a surface of about 160x280x2.5 cm and two square prisms 5x5x2 cm.

IMMEDIATE EFFECTIVENESS AND STABILITY OVER TIME

Immediate effectiveness

Table 2 presents the average values for the amount of product applied (APA), microdrop absorption times, and contact angle measured on the treated specimens for all tested situations.

Table 2. Average values for the amount of product applied (APA), microdrop absorption time as percentage of time required for absorption by the treated surface with respect to a control (MT) and contact angle (CA).

Stone	Product	APA (kg.m^{-2})	MT (%)	CA (º)
Limestone (A)	N	5.440	147	132
	H	5.090	108	109
Dolostone (D)	N	0.990	150	105
	H	0.910	108	106
Granite B (GB)	Q	0.064	96	85
	S	0.045	123	105
Granite D (GD)	Q	0.077	103	92
	S	0.063	125	108

The effect of the applied products was reflected in all the data obtained (see Table 2). It can be seen that, in general, all products were effective, and only GB stone treated with the silane product Q has a contact-angle slightly lower than 90º. This same sample also showed the lowest reduction in water absorption. In fact, with exception of GB-Q, all the tested treatments display values of microdrop absorption times and contact angle higher than 100% and 90º, respectively, the theoretical threshold for an effective treatment (Fig.1). The reduction in values between treated and untreated specimens, in terms of water absorption by the pipe method, ranges between 90 and 100% (Fig.2), with a clearly better performance of the polysiloxanes (H and S).

The 100% value of the microdrop absorption times after treatment is considered the minimum criteria for water repellency. In fact, an effective water repellent will always show higher microdrop absorption times because drops show a very regular spherical shape that renders evaporation more difficult than for those on the unpolished glass. This 100% threshold for the microdrop absorption times corresponds fairly well to the threshold of 90º adopted for the contact angle [6].

When contact angle and microdrop absorption times are plotted together (Fig. 1), almost all tested treatments fall in the first quadrant. This fact supports the idea that a contact angle of 90º and a microdrops absorption times of 100% seem to correspond to real threshold values of hydrophobised stones and therefore they are relevant criteria for assessing effectiveness.

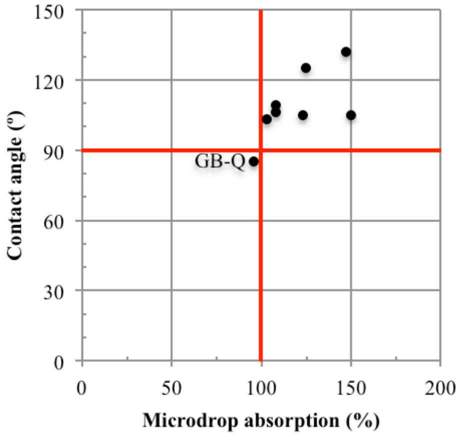

Figure 1. Contact angle and microdrop absorption times, after treatment.

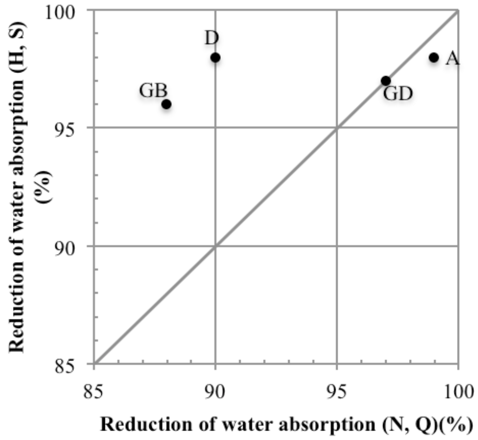

Figure 2. Comparison of silanes (N, Q) and polysiloxanes (H, S) in terms of water absorption by the pipe method.

When analysing the initial effectiveness, it is apparent that the silane product (N) proved to be more efficient on the carbonated stones (A and D), especially on the limestone A, while on the granitic varieties (GB and GD) the polysiloxane (S) was the most efficient one (Figure 3).

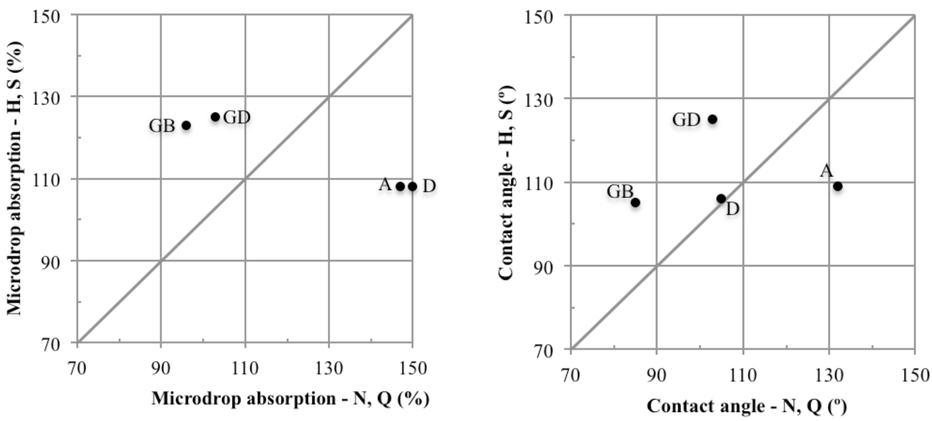

Figure 3. Comparison of silanes (N, Q) and polysiloxanes (H, S) in terms of microdrop absorption times (left) and contact angle (right).

Although the results have shown that the effectiveness of all treatments was influenced by the type of support, they also indicate that the effect of polysiloxane treatments appear to be less dependent upon the substrate than the silanes.

The influence of the amount of product was studied on the carbonate stone A treated with products N and H. The treatments were performed by brushing as follows: T1- one application; T2- 2 applications at a 7-day time interval; T3- 3 applications at 7-day time intervals; and, T4- 4 applications at 7-day time intervals. The treatments were performed on a slab specimen (160x280x2.5 cm) that was divided into four different areas, with a surface of approximately 160x70cm^2 for each number of applications. The absorbed product was determined by weighing the specimens in each step of the application procedure (Fig. 4). The influence of the amount of product involved in each treatment was assessed by means of the microdrops absorption times. Figure 4 shows that up to a certain amount of product there is an increased effectiveness tendency. Beyond that point, the application of higher amounts of product does not cause any further increment.

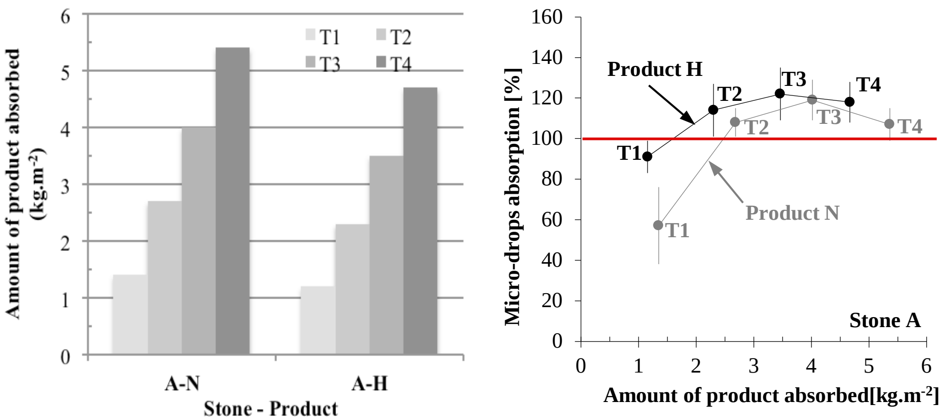

Figure 4.Treatments T1, T2, T3 and T4 performed on stone A. (Left) Amount of product absorbed; (Right) its influence on the superficial water repellent effect assessed by microdrop absorption times.

Effectiveness stability over time

Table 3 presents the average results of the microdrop absorption times, contact angle and water absorption by the pipe method before and after artificial (GB and GD) or natural exposure conditions (A and D). Figure 4 is a graphical representation of the situation before and after exposure as reflected by the changes in contact angle (CA) and microdrop absorption times (MT). The data obtained show that superficial water repellency was substantially reduced for all samples with the exception of the limestone treated with the polysiloxane (A-H). This fact shows that a relatively short exposure time is sufficient to obtain a significant impact in the performance of the water repellent products, and may constitute a relevant argument to support the usefulness of the exposure tests when studying new products, or the existing products when applied to different types of substrates.

The artificial aging in the laboratory has also induced significant changes in the two parameters, thus showing that this aging method also has its merits. The two situations cannot be compared directly, since both substrates and application procedures were different, however, it is interesting to note that some similarity of values exist between both approaches, although its practical significance is difficult to assess. A similar general tendency of the contact angle reduction while water absorption was not significantly affected with aging had already been reported [2].

Table 3 – Microdrop absorption times (MT), contact angle (CA) and water absorption by the pipe method after 1 hour (WA), before (Be) and after (Ae) aging

Exposure conditions	Stone	Product	MT (%)		CA (º)		WA (cm^3)	
			Be	Ae	Be	Ae	Be	Ae
15 months of natural exposure	A	N	145	95	117	80	0.025	0.025
		H	120	123	97	110	0.075	0.050
	D	N	152	9	128	23	0.000	0.000
		H	104	72	104	53	0.050	0.050
120 cycles of T and RH followed by 400h of UV radiation	GB	Q	96	78	90	69	n.d	n.d.
		S	119	95	110	90	n.d	n.d.
	GD	Q	99	87	94	70	n.d	n.d.
		S	127	95	107	92	n.d	n.d.

n.d – not determined

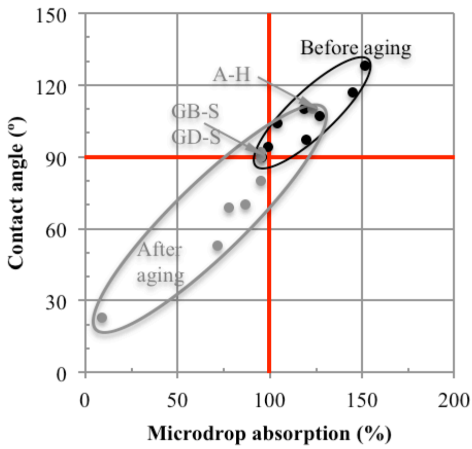

Figure 4.Comparison of the water repellency stability assessed by microdrop absorption times and contact angle, before and after aging (see Fig.1).

As mentioned, limestone A treated with the polysiloxane (A-H) stayed in the area of full effectiveness after exposure, while GB-S and GD-S, also treated with a polysiloxane product moved to the borderline of full effectiveness after the artificial aging, suggesting that the polysiloxane(s) had a general better performance on both stone types.

The measurement of the water absorption by the pipe method concerns the complete water repellent layer, not only the surface. Accepting that the alteration of the applied products progresses from the surface inwards it is reasonable to expect that the indicators of the surface water repellency (MT and CA) are the first to reflect the impact of aging.

The values measured for the carbonate stones show that the hydrophobic character was kept at the subsurface, as shown by the very low absorption obtained with the pipe test, thus showing that predicting the performance of water repellents requires a combination of tests to elucidate the full complexity of their performance.

CONCLUSIONS

The results obtained regarding the effectiveness of four commercial water repellents, two polysiloxanes (H and S) and two silanes (N and Q), on carbonate and granite Portuguese stones, have confirmed once more that the nature of the substrate and the amount of product applied influence the overall performance of water repellent products. Generally, polysiloxanes seem to perform better on both carbonate and granite materials.

The natural exposure and aging in laboratory showed to be valuable complements for the assessment of the durability of water repellent products, and the results demonstrate that 15 months of natural exposure is enough to see relevant changes in the performance of the water repellents.

The tests that directly evaluate the superficial water repellency (microdrop absorption times and contact angle) and the water absorption by the pipe method, which encompasses the subsurface zone of the tested stone, have highlighted that two distinct behaviours are identifiable, and therefore suggest that the combination of both types of tests is to be recommended for the assessment of the performance of water repellents. A clear hydrophobic effect (high CA and MT values) immediately after treatment is a favourable characteristic for any hydrophobic product. Their permanence in time is desirable, both in natural exposure and in laboratory aging simulations. However, if after some weathering the initial high values of these parameters are significantly reduced the water absorption value (WA) is still at a low value, this may indicate the permanence of the hydrophobic barrier provided by the product against liquid water ingress.

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