Hydrophobe VII *7th International Conference on*
Water Repellent Treatment and Protective Surface Technology for Building Materials
A.Elena Charola and J. Delgado Rodrigues, Editors
LNEC (Laboratório Nacional de Engenharia Civil), Lisbon: 2014 (179-188)

Testing new water repellent solutions to protect deteriorated granite

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SUMMARY: The evaluation of nano-particle based products to protect granite surfaces from water income is presented in this paper. Wettability, water absorption, drying behaviour and water vapour transfer were considered as the most relevant parameters for this evaluation. The effect of the application methods on the final performance was also tested. The results allow to consider that nanostructured products may present some advantages when compared with conventional water repellent products, namely on some common relevant harmful effects, such as colour changes, water vapour or liquid transfer during drying, but their effectiveness as barriers against water absorption in longer contact time may not be equally satisfactory.

KEY-WORDS: Granite, water repellent, superhydrophobicity

INTRODUCTION

Despite their low porosity and good mechanical strength, granites used in old monuments quite often show deeply decayed surfaces that require conservation actions. Consolidation is usually needed to mitigate erosion and stabilize material losses as a way to help preserve their intrinsic value. When exposed to external conditions, the use of a water repellent is also frequently used to complement consolidation treatments. Hydrophobization is sometimes used to prevent or reduce the penetration of water into the treated material to avoid or minimise its possible negative influence in the consolidation effect.

Silanes and oligomeric polysiloxanes have been used for protection of granite surfaces. Their organic composition is not generally felt as a relevant compatibility problem, but the changes introduced in the original drying and water vapour permeability characteristics of the material may result in harmful effects in the short or long term. After treatment, the materials dry more slowly, may be less permeable to water vapour transfer and colour may perceptively change. These drawbacks must be assessed and balanced when making the selection of a product to be used in practice.

During the last decade, water repellent treatments have been extensively used in practice to protect several types of materials, however, they may potentially induce damage, in particular when the income of water to the treated surface cannot be totally controlled, and therefore, new solutions based in different concepts have been developed and found to be very promising, even for the use in cultural heritage objects [1, 2, 3, 4].

The simulation of the natural “lotus effect” found in nature was used to develop new products for the protection of stone surfaces. Currently, several products using the superhydrophobicity principle aiming to produce self-cleaning surfaces or more effective water repellents exist in the market. Regular patterns and extreme micro or nano-roughness are key-parameters to produce a coat with high hydrophobicity properties under a sol-gel process. These aspects are developed at a nanoscale. The application of this type of non-wetting coatings over decayed polymineralic rock surfaces, characterized by the presence of fissures and cracks is the objective of the present paper.

RESEARCH AIM

The purpose of this research was to study the action of a new commercial formulation applied on decayed granite samples and tested in laboratory conditions.

In this initial phase of the study, the product was applied on a single variety of slightly weathered granite keeping the original roughness produced by the cutting action, without any special preparation to smooth that roughness. The design of these protection solutions may require the formation of coating layers with special characteristics and may require specific application procedures to reach those characteristics. To find the best procedure for the laboratory study, three different application methods were used.

Water repellency proprieties were evaluated by classic indirect methods, using water properties on a comparative basis. This evaluation is performed step by step, due to the fact that some tests are very time consuming and are only justified if a first level of performance is reached in the first testing step.

MATERIALS AND METHODS

Materials

For the study, one variety of granite collected at an outcrop near Evora was used. Granites with similar characteristics are also found in the Cathedral of this city. From a macroscopic point of view, it is a yellowish material with characteristic white veins that confer an evident heterogeneity. It can be considered as a slightly weathered material. Its most relevant characteristics are presented in Table 1.

Table 1. Porosity and water absorption characteristics of the tested granite.

Open porosity (%)	1.8 - 1.9
Maximum water content (%)	0.7
Water absorption by capillarity coefficient (**x 10^{-2}**, $kg.m^{-2}.h^{-0.5}$)	24-27
Water absorption (48h) (%)	0.6
Real density ($kg.m^{-3}$)	2655
Bulk density ($kg.m^{-3}$)	2604

The product used as a protective was “Aquashield Ultimate” (AQ), previously commercialized as “Tecnadis PRS Effect”. Additional information is available in the web page of the company (http://www.tecnan-nanomat.es/).

According to the information available from both the manufacturer and the seller, it is a nanotechnology based water repellent with very high performance that offers a total protection for every type of building material on facades, including porous and low porosity substrates, such as granites. It is a dispersion of nanoparticles treated with tension-active agents in acetone. The water repellency properties are considered to be due to the characteristics of the nanoparticles with very small diameter and high specific surface area. The composition of the particles forming the product (and thus the coat) is not reported.

For comparison, some specimens were treated with a conventional product, an oligomeric siloxane in white spirit (8% concentration) that promotes the formation of a polysiloxane (P) after complete hydrolysis.

Preparation of specimens

Two types of samples were prepared: cubes of 5x5x5 cm and thin slabs 5x5x1 cm. The cubes have their lateral surfaces sealed with an epoxy resin to have better defined application and testing conditions.

The technical sheet prepared by the manufacturer recommends applying the product by spray (without or under low pressure). Other methods, such as a brush or roller, are also indicated as alternative application methods.

In our laboratory experiments, products are usually applied to specimens by direct contact with the liquid during a very short period of time (in seconds) to control the precise amount of product absorbed and retained after curing. However, since conditions used in practice are different and to follow the manufacturer's recommendations, two other application methods were used, by brush and by spray.

The product is "ready to use", and dilution is not recommended. Successive applications are admitted and at least two are recommended. Twenty four hours is the interval indicated to produce the water repellence effect. Two specimens per testing condition were prepared.

Table 2 shows the total amount applied and the dry matter retained after treatment with Aquashield Ultimate (AQ). The application of 60ml/m^2 (15ml /specimen) was used as the criterion to determine the end of the treatment. For about twenty days the specimens were kept in laboratory conditions and then dried (at 60ºC) to compute the *dry mass* after treatment.

Table 2. Product applied and dry matter in the protective coating (AQ)

	Application method		
	brushing*	**direct contact*** (immersion 1mm, for 10 sec)	**spraying**** (until wet)
Product applied (g/m^2)	54 – 96	34 - 37	47 – 49
Dry matter (g/m^2)	3.7 - 7.8	3.7 - 6.5	3.8 - 3.9

* applied four times in sequence, at 5 minutes interval ; ** applied two times

Similar conditions were also followed to prepare the thin slabs used to determine the water vapour permeability. These same slabs were also used to evaluate the static contact angle.

In the case of the oligomeric siloxane (P) the product was applied only by brushing.

Evaluating effectiveness and harmfulness

Conventional tests were used to evaluate the water repellency effect promoted by the product and the "*triple capillarity test*" was used to estimate the thickness of the layer impregnated by the product [5, 6].

Water absorption by direct contact gives complementary information on the wettability of the surface and on the suction properties changes in the zone immediately below the surface. Besides other current methods used to evaluate water absorption such as *microdrops absorption* or *water absorption by the pipe method* currently used for this purpose, the *sponge method* was also used as it is very simple and particularly sensitive when performed under laboratory conditions. In this test a sponge used as a water reservoir is placed in direct contact with the treated surface and the water transferred into the stone over time is measured. The method as initially proposed [7], stipulates 30 seconds as the contact time. In this study, the interval was extended to 2 minutes to cope with the low absorption characteristics of the original stone material, before and after treatment.

The "*static contact angle*" measures the wettability the stone surface and allows identifying the hydrophobic characteristics of the applied product. The test is carried out under a binocular microscope and the measurements were done on photographs taken with a camera or directly with the use of a micrometer (measuring both the height and the contact line of a water droplet on the surface). The droplets were let fall from about 1-cm distance to the surface.

"W*ater vapour permeability*" and "*drying behaviour*" were considered as very relevant to evaluate the changes on the original characteristics of the granite specimens. The protocols of testing were based on the RILEM Recommendations [8].

In this particular case, chromatic changes on the appearance were not considered as very relevant for this preliminary evaluation of the treatment. In fact, visual evaluation allows seeing minimal colour changes and, in this particular case, they are completely disguised on the natural heterogeneous colour patterns due to the presence of several types of minerals.

RESULTS AND DISCUSSION

After the application of the AQ product via the three different methods ("direct contact", "brushing" and "spraying") the nanoparticles coatings were formed.

Water absorption of the treated surfaces

Figure 1 presents the values obtained in the triple capillarity test [5, 6] for samples treated with the nano coating (AQ) and the oligomeric polysiloxane (P) products. The graphs of the reversed condition indicate that a lower amount of water was absorbed once the stationary regime is reached. This reduction results from the presence of the hydrophobized layer and is proportional to its thickness. The thickness of the treated zones was computed using the formula (a), according to Delgado Rodrigues et al. [5, 6].

$$e = \frac{\Delta Q_t \,.P_s}{Q_t \cdot \gamma_{ap} \cdot S} \qquad \text{(a)}$$

Where,

ΔQ – difference in water mass absorbed at time *t*, in the untreated and in the test with the treated surface upwards [g];

P_s – dry weight of the specimen [g];

Q_t – amount of water absorbed by the untreated specimen at the time *t* [g];
γ_{ap} – stone bulk density [g/cm^3];
S – prism cross section [cm^2]

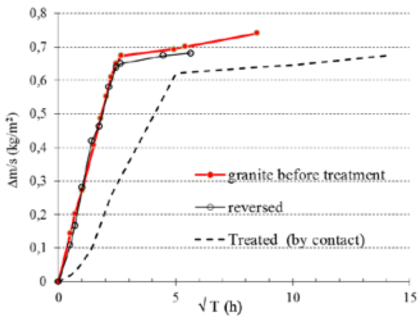
The values obtained are very similar and around 1 to 2 mm. The thickness of the nano-coating is always very small, as expected for a product that is intended to increase the surface micro-roughness. The value obtained with the conventional water repellent treatment (P) is around 1.6 mm.

The water absorption properties of the protected surfaces (Fig. 1) clearly indicate different behaviors of these protection coatings or layers. The surfaces treated with AQ change their absorption behavior with a clear reduction in the absorption rate in the initial period of the test, but rapidly increment the absorption rate to values similar to the untreated surfaces. This behavior usually occurs when the treated layer is very thin as confirmed by the low values determined in the triple capillarity test.

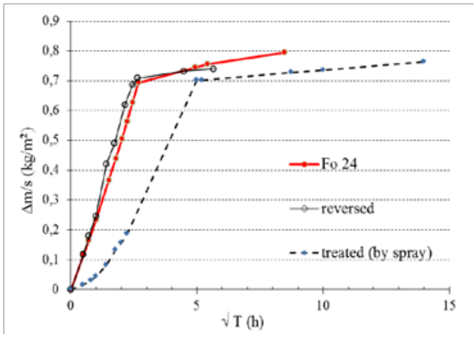
It should also be mentioned that acetone has a certain hydrophobic effect, and we could not separate this effect from the effect attributed to the nano-composite product itself. Nonetheless, it is clear that the hydrophobic effect of this product is to be ascribed to the very high contact angle, which reduces substantially the surface wettability, while this effect may be vulnerable if subjected to longer contact times with liquid water. The conventional water repellent product (P) changes completely the absorption kinetics, as seen in the respective graph. The treated surface acts as a barrier and penetration through the treated material is significantly slowed down for a much longer period, certainly due to the presence of a thicker hydrophobized layer.

Water absorption with the sponge method complements the evaluation of the surface absorption capacity. Besides quantification, it is possible to see that after the contact with the wet sponge no signs of wetting are visible and the appearance of the surface is uniform. Completely different situation can be observed on untreated surfaces where the granite rapidly gets darker due to the water absorption (see Fig. 2). The computed values of water absorbed by contact from the wet sponge presented in Table 3 indicate a lower absorption of the protected surfaces when compared with non-treated granite. However, the test was not able to discriminate the application conditions or even the two products.

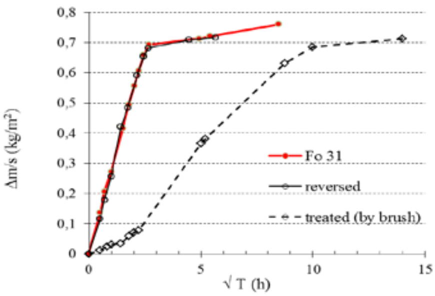
Static contact angle is very informative and relevant to evaluate the wettability of the surfaces treated with these two water repellent products. The values obtained in surfaces treated with the conventional water repellent product (P) indicate that they are hydrophobized since the contact angle is higher than 90º (usually considered as the threshold between wetting / non wetting behaviours), but they are rather close to this limiting value. The protection conferred by the use of the product AQ is far more effective. Characteristically the contact angles measured are higher, with an average value around 120º. Some examples are presented in Figure 3.



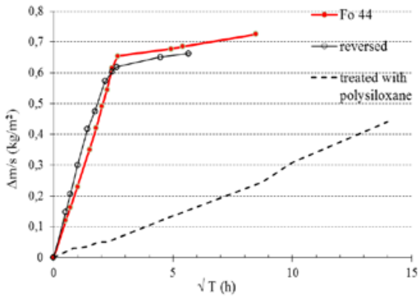
a) specimen treated with AQ by contact; estimated thickness of the treated zone – 1.2 mm.



b) specimen treated with AQ by spraying; estimated thickness of the treated zone – less than 1.0 mm.



c) specimen treated with AQ by brush; estimated thickness of the treated zone – less than 1.0 mm.



d) treated with P (by brush); estimated thickness of the treated zone – 1.6 mm.

Figure 1. Water absorption kinetics in the triple capillarity test before and after treatment with AQ and P. Red line with solid circles corresponds to the untreated specimen; Dashed line corresponds to treated face in contact with water; Black line with open circles corresponds to treated specimen with the treated face upwards (reverse).

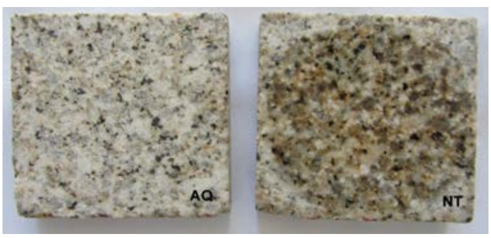
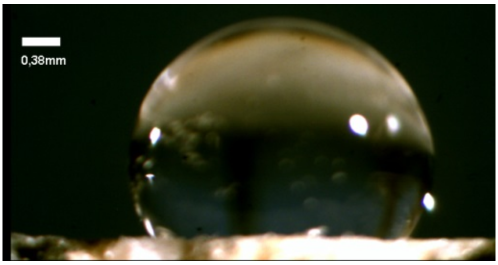
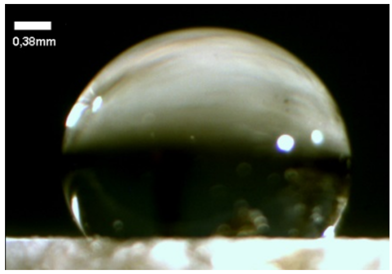


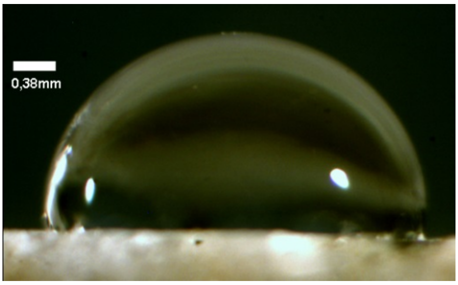
Figure 2. Specimens treated with AQ (left) and untreated (right), after 2min of contact with a wet sponge.



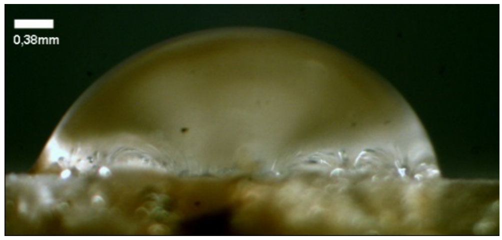
a) treated with AQ (by brush).



b) treated with AQ (by spray).



c) treated with P.



d) Granite non-treated.

Figure 3. Contact angles in specimens protected with AQ (treated by brush and by spray) and unprotected (d).

Table 3. Values of the *static contact angle* and water absorption with the *sponge method*

	Product AQ			Product P (brushing)	Granite untreated (NT)
	brushing	direct contact	spraying		
Static contact angle (θ)	116º ± 4º	120º ± 5º	120º ± 6º	96º ± 3º	66º ± 7º
Water absorption by contact for 2 min. (x10 kg/m^2)	0.29	0.31	0.35	0.29	0.74

In Figure 4 values of water absorption with the *sponge method* versus *contact angle* are represented. This relation has been tentatively called *wettability*. The effectiveness of the treatments is evident when compared to the original characteristic of the stone and no evident differences can be identified among the three application methods considered in this study. The values of the nano-coating show higher variation range on both characteristics, while P is apparently more homogeneous, but the smaller number of measurements performed in this case may partly explain the difference.

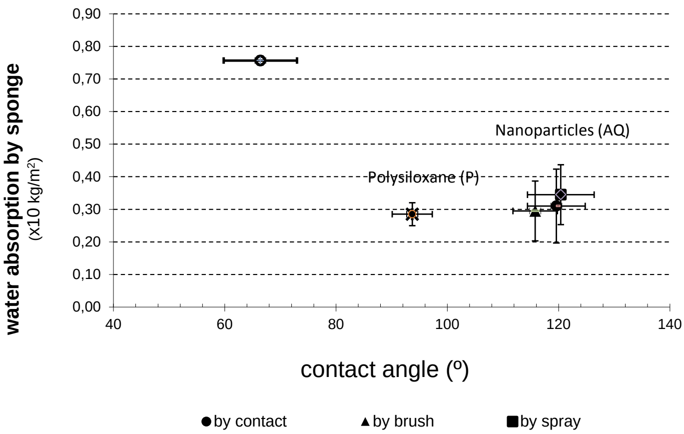


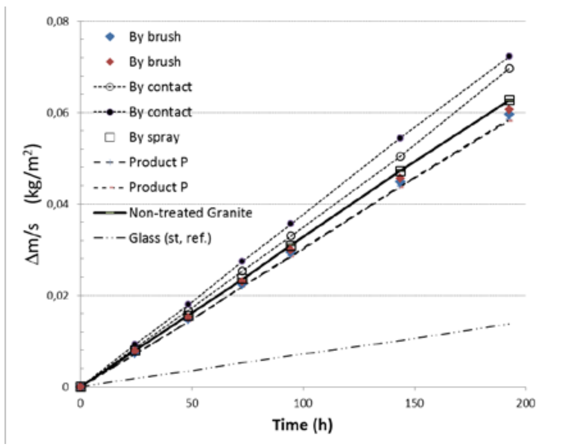
Figure 4. Water absorption by contact sponge vs. contact angle of the granite surfaces with and without protective coating.

Drying behaviour and water vapour transfer

These two characteristics are very relevant in the assessment of the performance of any conservation treatment, and in particular when water repellence effects are involved. Manufacturers usually claim that water repellents do not change water vapour transfer, or that they do no contribute to make the surface more impermeable after treatment. However, in spite of the fact that improvements have been made, quite often experimental results show that these harmful effects are also present. Changes promoted on drying upon treatment are also a concern, and in particular when salts are present the effect of a slower drying can be particularly harmful. Table 4 presents the effect of the application of the products (AQ e P).

Table 4. Values of water vapour permeability with and without protective treatments.

	Water vapor permeability coefficient (x 10^{-9} kg m^{-1} h^{-1} Pa^{-1})
Product AQ (brushing)	1.82 - 1.86
Product AQ (direct contact)	2.17 - 2.20
Product AQ (spraying)	2.00 - 2.08
Product P (brushing)	1.74 - 1.79
Granite untreated (NT)	1.89



Note: Test performed with the “dry cup method”.

The results obtained indicate a slight decrease of water vapour permeability due to the application of product P but this effect is almost negligible in the case of the AQ product.

Concerning drying (Fig. 5), the results indicate that also in this aspect the nano-coating applied by any of the tested methods has advantages when compared with a conventional water repellent product such as P, but drying remains faster for untreated surfaces.

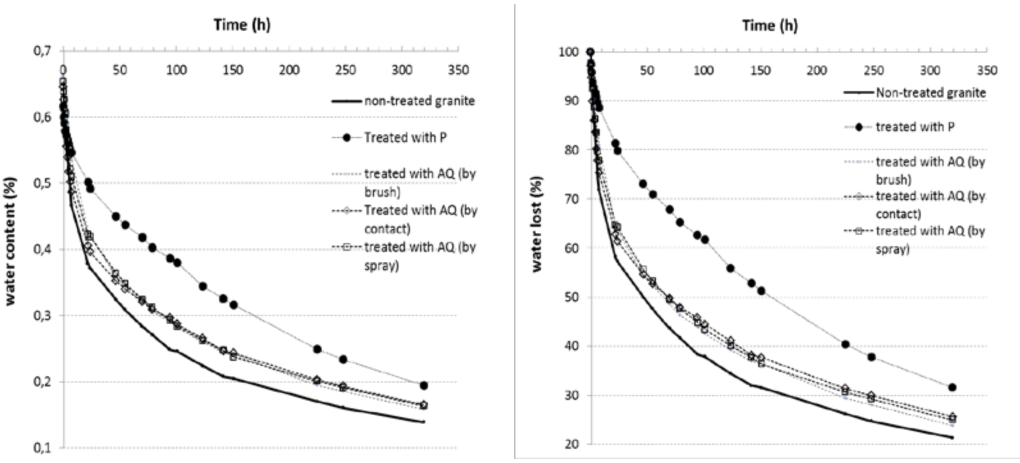


Figure 5. Drying behavior of granite surfaces with and without protective coatings. Note: Tests performed at 70% RH and 20ºC.

CONCLUSIONS

In this study a commercial nanoparticle based protective treatment was tested on slightly weathered granite. The information about the composition of product is unavailable and the protective layer formed has as yet not been characterized, but the main objective was to evaluate its ability in forming a superhydrophobic layer and/or conferring water repellency to the treated surface.

The measurements performed confirm that high contact angles are obtained by drops applied to the treated surfaces and a decrease of their wettability properties. The water absorption behaviour under the capillarity test is typical of specimens having a very thin treated layer, a fact that was confirmed with the values determined by the triple capillarity test.

The product reduces water evaporation during drying but this effect is less pronounced than that observed for a conventional oligomeric polysiloxane. Water vapour permeability after protection is similar to the unprotected granite. Color changes due to treatment are negligible and are not perceptible with the naked eye.

The nanoparticle based product applied uses acetone as a solvent and it can migrate (alone or with nanoparticles) easily into fissures, such as found in the granite tested. The rapid increase in the absorption rate when the specimens are in contact with liquid water suggests that the hydrophobic protection is very superficial and that longer contact times will break down the “barrier effect” it produces on the surface.

Future research is needed to elucidate other relevant aspects, such as the nature and structure of the coatings, the depth of the hydrophobic effect, the dynamics of water absorption, any delayed harmfulness that may develop subsequently and, their durability.

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