12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

A CRITICAL POINT OF VIEW AND RECENT STUDY WITH INNOVATIVE TOOL TO EVALUATE THE PENETRATION DEPTH OF A WATER REPELLENT TREATMENT ON POROUS INORGANIC MATERIALS

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Abstract
Water repellent treatment is one of the most important interventions usually carried out in the conservation of stone materials. It is essential to choose a suitable product and then to ascertain its effect on a medium and long term basis. Obviously only after experimentation, first in laboratory and after in *situ*, the behavior of the treatment can be determined. Recently the CEN TC 346 has been trying to establish a common methodology to test in laboratory water repellent products applied to porous inorganic materials. The methodology and time of application can strongly influence the depth of penetration of a treatment into a porous structure. In this paper, a preliminary review by analyzing and highlighting some crucial elements in the study of water repellent treatment in stone specimens has been carried out.. Besides, a comparison has been made between the results of our recent studies of water repellent treatment on a sandstone and a biocalcarenite with the aim of showing the close correlation between the time of application of the product and its penetration depth on stone evaluated by Unilateral NMR depth profile and capillarity absorption .

Keywords: stone treatments, water repellent, penetration depth

1. Introduction

Water repellents are used to prevent or to reduce water penetration into stone and thereby reducing the decay of the materials. As a consequence it is essential to choose a high quality water repellent product and then to ascertain its effect on a medium and long term basis. Obviously only after experimentation the behavior of the treatment can be determined. As it is well known, it is very difficult to carry out the experimentation in *situ* because numerous variables must be taken into consideration. For instance, stone properties can vary widely for the same type of stone depending from which part of the quarry the block of stone was taken. For in *situ* experiments stone properties depend both on the condition of the stone surface and the atmospheric environment.
For this reason, it is easier to perform experimentation in laboratory where the experimental conditions can be better controlled. Obviously, to obtain a direct comparison of the results from several studies, it is necessary to have a protocol regarding the most important parameters of evaluation and the methods of application of the water repellent treatment. Besides, there are other factors that are difficult to

control, such as the use of the manufactured water repellent products which do not comply with standard requirements. Consequently when a laboratory tries to find a high quality water repellent treatment, the most important questions to be considered should be as follows: how should the coating be applied? how long should be the application time? how much should be applied? and how important is it to evaluate the water penetration depth of water repellent treatment?
At the moment in Europe the framework of CEN TC 346 a team group entitled "Evaluation of methods and product for conservation works on porous inorganic materials constituting cultural heritage" are currently drawing up a protocol for the standardization of test methods that should be used to evaluate the behavior of a water repellent.
Many papers since 1990 have provided a critical review on the methodology of application of protective treatments (Delgado Rodriguez and Charola 1996, Charola 2003, Pien and Vanhellemont 2003).
In this paper, a preliminary bibliographical review is reported in order to understand what are the most popular systems of application of water repellent products and if these methods of application are the same results on every kind of stone and for every kind of product. Besides, a comparison has also been made between the results of our previous and recent studies of water repellent treatment on sandstone and biocalcarenite with the aim of showing the close correlation that exists between the time of the application product and its effect on stone.

2. Methodology of application of the water repellent.

Among the 100 papers reviewed the following different application techniques were taken into consideration: capillary rise absorption (37 papers), brushing (23 papers); total immersion (14 papers), spraying and cream (7 papers).
In 21 papers, the application techniques were not specified, and only in some of these the amount of product after drying was indicated.
Besides, it should be noted that:

- the time of application is extremely variable and in most cases does not take into account the different lithotypes and chemicals in the frame of the same research;
- preliminary conditioning of the samples is often reported, but it is carried out in very different conditions;
- the amount of product in the sample is often reported, but the conditions specified are very different;
- the evaluation of the efficiency is reported in relation to the capillary water absorption and more rarely in relation to contact angle and the water absorption at low pressure (Karsten tube or pipe);
- generally treatments by capillarity, brush or spray are carried out on only one face of the sample, with the exception of one paper which involved 4-6 sides of the specimen.

Matteoli (1993) and Charola (2003) compared all the above mentioned methods to determine which one gave the most reproducible and homogeneous results and consequently came to the following conclusions.

Brushing was discarded because it depends upon the skill of the operator. In fact, the amount of product applied cannot be easily controlled. As a consequence, the treatment was not homogeneous resulting in different degrees of thickness of the product in the same sample.
Spraying was also discarded because the sample being of such a small dimension it was inevitable that much of the product was dispersed in the surrounding atmosphere and an insufficient quantity was applied to the sample.
Totally immersion of the specimen produced homogeneous penetration, but had a drawback of creating air bubbles .
The method producing the most homogeneous and reproducible results was the capillarity treatment, where the sample was placed on multilayer filter paper soaked with protective solution. In this way, application of various protective products was sufficiently uniform avoiding problems related to the skill of the operator performing the treatment.
In the case of application procedures some researchers (Cnudde *et al*.2007,) preferred to simulate in situ application methods by using the spraying or brushing techniques. But the small dimensions of the testing specimens drastically reduced the possibility of making this a representative sample and the extreme difficulty of applying the product in a reproducible manner eliminated the advantages of this approach.

3. Which is the best time of application? What is the optimum quantity to be applied to the samples of the various lithotypes?

The type and the extent of protection offered by the various products to be tested can easily vary according to the quantity of product applied. Therefore, the use of the same quantity of different protective products does not necessarily imply the achievement of similar protection. The protection might also vary in the case of different lithotypes, since each lithotype requires a specific adequate quantity of protective material.
According to the producers a short time is advisable because it simulates in situ application conditions quite well. A drawback in simulating in *situ* conditions is the difficulty to have reproducible conditions. In fact, the external environment presents variable thermo-hygrometric parameters, such as temperature and relative humidity, which could influence in various way the efficacy of application and give some negative results.
A difference in the duration of the treatment corresponds to a different depth of penetration and a different degree of effectiveness. In some cases, treatments applied by brush method continued up to saturation (Boutin 2001, Calia *et al*. 1996) or by repeating the treatment several times (Daniele and Taglieri 2010).
In other papers the immersion method lasted a few seconds (Lubelli and van Hees 2004), and for a very long time(Bofeltd and Nyman 2002). Short times were used in order to obtain a homogeneous absorption but also to handle an amount of product comparable to in *situ* conditions while long times were chosen in order to obtain maximum results.
Treatments by capillary absorption were conducted for a few seconds (De Clercq and De Witte 2002, Riecken and Sasse 1997), or were prolonged for longer times (Johansson *et al*.2009, Casadio and Toniolo.2004).

It is note that different stone porosities strongly influence the degree of protection , and the amount of product absorbed by capillarity in the same application time. In a large experimental research carried out by the Italian Commission for Standardization UNI-Normal (Commissione Normal 1993; Appolonia *et al* 1995) the degree of protection calculated after 24h of capillarity water absorption was 48%, 91%, 98% on samples of marble (open porosity P% 1), sandstone (P %7), limestone (P% 35) respectively when the duration of application was 1h by capillarity product absorption.
The protection degree by capillarity was calculated according to the following formula

$$PD_C\ (\%) = \frac{Q_{bt} - Q_{at}}{Q_{bt}} \cdot 100$$

Q_{bt} amount of absorbed water of untreated specimen
Q_{at} amount of absorbed water of treated specimen

Moreover the same type of product applied on two different stones under the same conditions can produce different degree of penetration depth. In (Esbert 1992), for instance, in the Hontoria limestone, which had an open porosity of 23% a product applied by capillarity absorption penetrated up to 5 cm in depth, while in the Laspra dolostone, which had a higher open porosity greater than 30%, the same product applied under the same condition only reached a depth of penetration between 5mm and 10 mm. This was directly related to the size of the pores that make up the pore system of each rock.

4. How important is it to evaluate the penetration depth of the water repellent treatment?

As it has been previously mentioned over the last years many papers on the evaluation of hydrophobic treatments have been published. In almost all of these papers to estimate the quality of treatment the measurements of numerous parameters were carried out, while the depth of penetration was often overlooked (only 10 % of all papers examined were considering it). This parameter is generally considered in the case of consolidation treatments because in this case is recognized to have a primary role for consolidation efficiency.
Regarding the need to evaluate the penetration depth researchers are divided into two groups: those in favor and those against.
Who is usually opposed claims that water repellent is working on the surface of the material consequently a great depth of penetration is not necessary to guarantee a good efficiency of the treatment. For instance, in (Pien 1985) it showed that in the case of alkylpolysiloxane applied to calcareous stone, a great extent of impregnation (about 45 mm) caused a decrease of the water vapor conductivity preventing the permeability of the material.
On the contrary, between those in favor of penetration depth, (Hoyneborne 1932), already reported that "*a common cause of failure of stone preservatives if that, even in porous materials, and under the most favourable conditions, the preservative penetrates only to a relatively small depth, and a surface skin is formed which differs in physical*

properties from underlying material". Over the last ten years several points of view have explained more clearly the importance of the penetration depth in order to assure the best efficiency of the water repellent treatment.

Some results about residual efficiency of ancient water repellent products applied to calcareous stones were reported by Vallet and Vergès-Belmin (1996). In this study the impregnation depth was used as a parameter in a theoretical geometry model to describe the absorption phenomena in stone. In particular, it is written that ".....*and the depth of impregnation could be significant to evaluate the importance of conservation operations on treated historic stones*".

In "La protections des pierres-Guide sue les hydrofuges de surface", 2000, numerous observations regarding the best conditions to improve the durability of the hydrophobic products were reported. According to the author, usually the optimum degree of water repellent impregnation is achieved when the amount of product prevents water penetration thereby allowing vapor leakage. Therefore, if the water repellent product forms a thick layer on the stone surface the durability of the treatment will be unsatisfactory, *"Si la solution appliquée pénètre peu dans le matériau poreux (exemple de produits filmogènes), ou si la réaction de réticulation ne s'effectue qu'en surface, la durabilité sera faible"*. The best depth of penetration usually ranges from some millimeter to 2-3 centimeter depending on the type of stone. Bromblet and Mertz (2002) state that in most cases, the increase of the penetration depth of the water repellent is important "D*ans le plupart des situations, accroître la pénétratione profondeur d'un produit hydrofuge constitute un objectif important*".

"*The degree of penetration and the distribution of polymers inside the porous matrix of stone is an important parameter when evaluating the efficacy and durability of treatments"*.

5. Experimental

In a experimental study we have applied a water repellent (dimethylsiloxane in white spirit) on sandstone and biocalcarenite samples by capillary rise at different times and the results of capillarity absorption were evaluated .On the same samples were carried out also measurements by unilateral NMR with the aim of evaluating the depth of penetration.

The two lithotypes used were chosen because of the different open porosity values and the different chemical matrix. Sandstone's total porosity was about 10% and a unimodal porosity distribution with a radius ranging between 0.064 and 1 µm , biocalcarenite 's total porosity was about 35% and an unimodal porosity distribution with a radius ranging between 0.25 and 4 µm. In the case of sandstone 10 specimens of size of 5x5x2 cm were used for each application time used. In the case of biocalcarenite 4 specimens of 5x5x2 cm were used, because the specimens analyzed produced an equal capillary water absorption curves , a smaller number of samples were considered sufficient quantity. The water repellent used was a dimethylsiloxane in white spirit. The hydrophobic treatment was applied according to the UNI 110921 by capillary rise and short and medium range application times for 5 seconds, 600 seconds, and 1800 seconds respectively.

Before and after hydrophobic treatment, the determination of capillary water absorption was carried out using the European standard EN 15801. In Figure 1-2 are reported results of capillary water absorption curves of sandstone and biocalcarenite .
In Tab. 1 the degrees protection by capillarity (PD_c), calculated at 1h, 24 h, 48 h respectively, are reported.

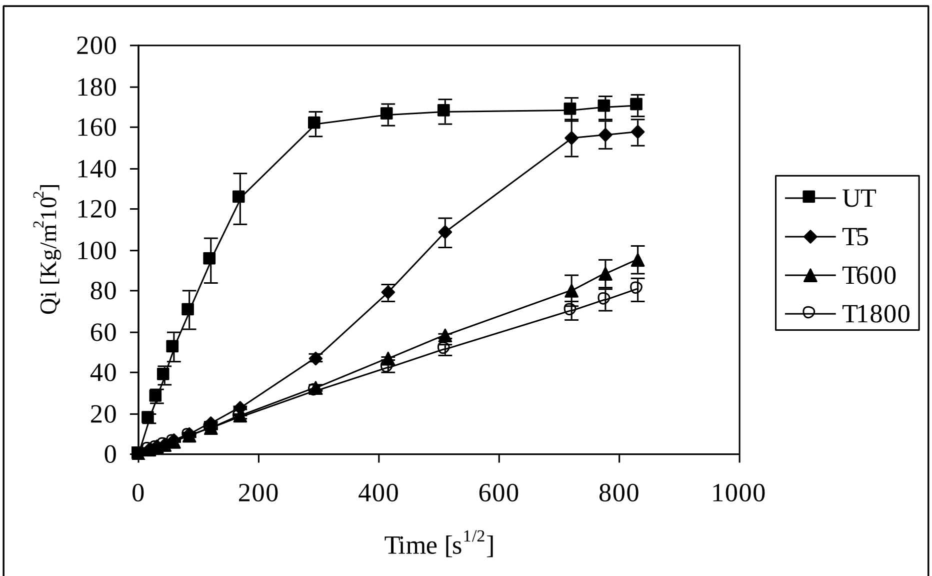

Figure 1. Capillary water absorption curves of of sandstone, The average values (Q_i) reported here, were calculated of 10 samples of sandstone.

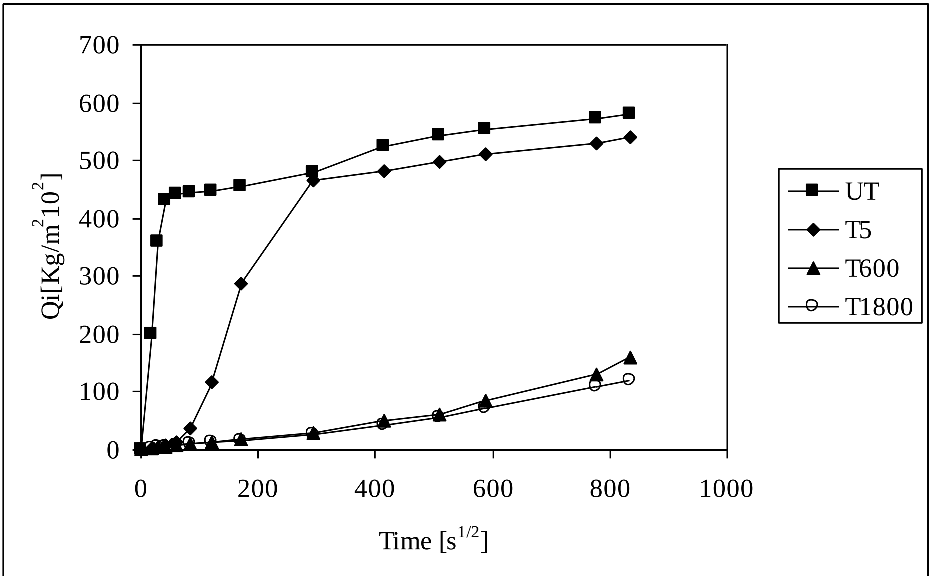

Figure 2. Capillarity water absorption curves of limestone The average values (Q_i) reported here, were calculetd of 4 samples of biocalcarenite with a dispersion of 0.5%.

Samples	PD_c%(1h)	PD_c%24h	PD_c%(48h)	Application time (s)
Sandstone UT	---	---	---	0
Sandstone T5	84	74	46	5
Sandstone T600	83	80	64	600
Sandstone T1800	85	81	69	1800
Calcarenite UT	---	---	---	0
Calcarenite T5	97	3	2	5
Calcarenite T600	98	94	93	600
Calcarenite T1800	99	96	95	1800

Tab.1 Protection degrees by capillarity calculated at 1h, 24h, 48h .

At short water uptake times, the absorption of water was reduced in all treated samples, and the value of protection degree was found to be very high. On the contrary, at longer time, the amount of water absorption by capillarity of the treated samples at 600 and 1800 second was found to be very lower than that absorbed by the samples treated for 5 seconds . Treatments performed at 600 and 1800 seconds seem to produce similar effects as shown by the absorption capillarity curves.
The same biocalcarenite and sandstone samples were analyzed, moreover by unilateral NMR. (Di Tullio *et al*. 2011). The unilateral NMR device allows the total amount of water inside porous material to be evaluated. Depth profiles of the hydrogen content inside specimens up to 1 cm depth were performed.

In Figure 3 and 4 the NMR depth profiles of the water saturated untreated stones are compared with the profiles obtained on water saturated stones treated for 5 seconds, 10 minutes, and 30 minutes respectively.

On Y axis is reported the amplitude of NMR signal that is directly correlated with the amount of water. On X axis is reported the depth of measurement inside the specimens treated with the water repellent product.

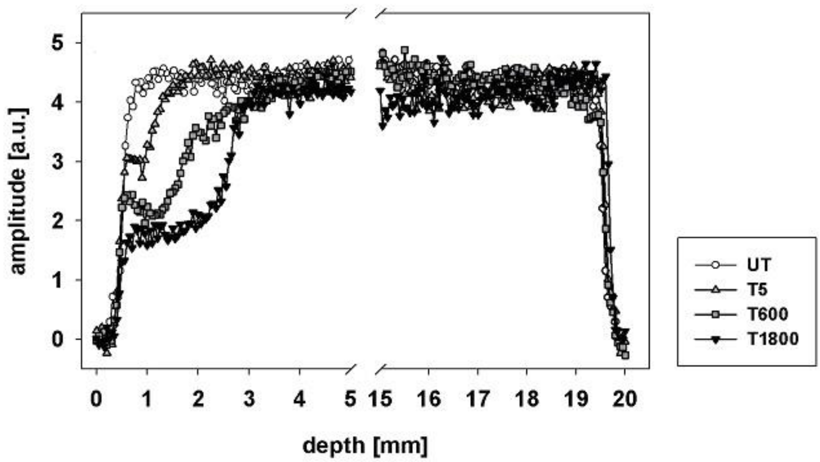

Figure 3. Depth profiles of sandstone. Profiles reported were obtained after making specimens absorb water from the treated side. T5, T600, T1800 indicates samples treated for 5 seconds, 600 and 1800 seconds respectively.

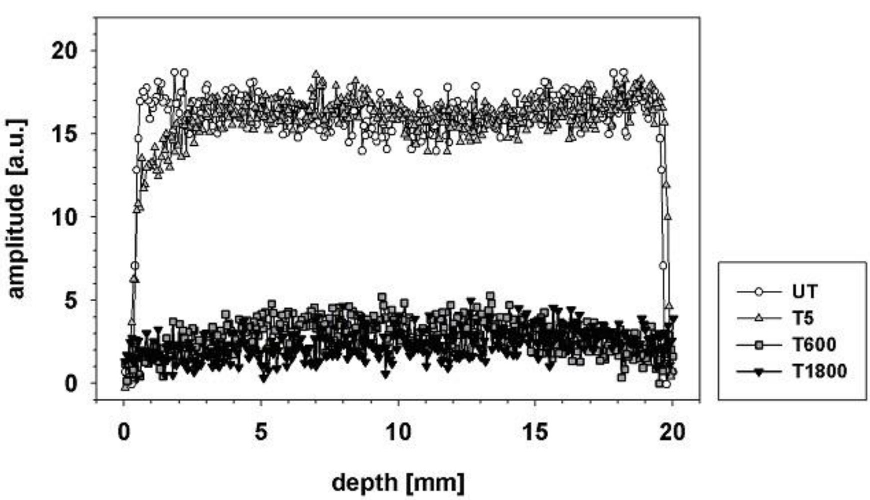

Figure 4. Depth profiles of biocalcarenite. Profiles reported were obtained after making specimens absorb water from the treated side. T5, T600, T1800 indicates samples treated for 5 seconds, 600 and 1800 seconds respectively.

In Figure 3, in the case of sandstone it is possible to note that the longer the time of application the deeper the penetration of the treatment is. In fact after treating for 5 seconds, the protective treatment penetrates up to about 500 µm . After treating for 600 and 1800 seconds, the protective treatment penetrated up to about 1100 µm and 2000 µm respectively.
In the case of biocalcarenite, see figure 4, the depth profiles did not show significant effects in the penetration depth between the samples treated for 600 and 1800 seconds respectively. These results are in good agreement with the results obtained by the capillary water absorption curves above showed.

5. Conclusion

In the most papers considered here, the application methodologies are often not well described and consequently it is very difficult to appropriately compare the results showed.
The choice of the methodology only in some cases is correlated with the surveys that they intend carry out or in relation to the case study which is under consideration.
The penetration depth for many years was considered an important property especially for consolidation purposes, but only recently it is being taken into consideration as a significant property to assess the effectiveness of a water repellent treatment which must be able to create a barrier towards rainwater and above all to atmospheric pollutants.
Probably the durability of the treatment is strongly influenced by the penetration depth.
An appropriate depth of penetration can be obtained by capillarity treatment performed for a long time or by repeated application by brushing or with particular methodology of application, i.e. creamy systems, which allow to reach good penetration also in *situ* applications.
In these last years it is note that brushing treatments increased considerably especially used for nano-structured products.
Besides, the results presented in this paper clearly showed that unilateral NMR is suitable to evaluate the depth of penetration of protective treatment. Furthermore, being Unilateral NMR a portable technique, a further step will be the optimization of this analytical measurements to be applied directly on building and monuments.

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