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Assessment of residual effectiveness for Water-Repellent treatments for building stones. Water absorption tests on the monumental complex Cathedral of San Zeno and the Baptistery of San Giovanni in Corte in Pistoia

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Abstract. Preventive and temporal planning of conservation is rather difficult to perform, especially concerning monumental stone buildings; the choices are often made after the degradation phenomena have already started. Many studies are looking for the reasons for this 'resistance'. In particular the present study, the result of a doctorate research, is focused on the most operational aspects: • quantifying the residual effectiveness of water-repellent protective agents used in past restorations; • providing elements in the drafting of maintenance plans for monumental heritage; • verifying where critical conservation elements reside. The test site has been the monumental complex formed by the Cathedral of San Zeno and the Baptistery of San Giovanni in Corte in Pistoia, where the Contact Sponge Water Absorption Test (UNI 11432:2011), typically used as treated/untreated test was employed on three lithological types (white marble, serpentine and Tuscan grey sandstone) as comparison test between treatments carried out at different knows times. The test campaign was conducted by Mila Martelli with the involvement of Superintendency of Archaeology, Fine Arts and Landscape; University of Florence DiDA, DST-LAM, Department of Chemistry and, in the phase of organization of the monitoring, with the involvement of Dr. Maria Jose' Ybañez Worboys, art restorer. The results of this research must be read in consideration of the fact that it is an ex-post survey, for which not all factors have been kept under control from the beginning, but for which it was possible to make assumptions. This study illustrates the methods and the first test results obtained which show a rather rapid decline in the effectiveness of water-repellent treatments, already a few years after their application.

1. Introduction

One of the themes always proposed and recommended by the Restoration Charters both as a critical / theoretical reflection as well as, above all, as a cornerstone of the conservation practice is that of the documentation of the conservation activities, particularly as regards the experimental or highly specialized one. This scientific obligation is not always reflected in the testimony and memory of the interventions carried out. This essay synthetically retraces a specific activity conducted on outstanding and very well known Italian monuments which also represents a peculiar methodological path, aimed at documenting the results of latest generation systematic investigations conducted at a distance of times after the application of specific substances for specialist restorations. The essay is therefore also a critical reflection and an operative proposal in view of a more extensive application of the deferred investigations both in terms of method and methods and techniques.

The investigation into the residual effectiveness of conservative treatments of decorated architectural surfaces appeared appropriate to address some issues of preventive conservation such as the lack of 'in situ' monitoring years after treatments, which is influencing the management of preventive conservation of cultural heritage. The study focused on the possibility of 'measuring' and 'quantifying' the residual efficiency of protective treatments used in the conservation of stone monuments after a certain time from their application, and therefore their 'durability'; but the big challenge of this research has been to perform this assessment exclusively by mean of 'in situ' tests and in real condition, thus tackling some issues that pertain the architectural scale. This research therefore necessarily brings with itself some approximations inherent in being an ex-post survey, in which not all factors could be kept under control from the beginning, but for which it was possible to make hypotheses: for example, the quantities of product absorbed at the various points are not known, nor how the products were applied; accordingly, it dives into reality and contingency reading the actual yield of the treatments on the stones examined and not the theoretical one obtained in laboratory tests under controlled conditions. As a result, a simple test as the contact sponge water absorption test (UNI 11432: 2011) has been stressed and rather used as a comparison test between treatments with different, and known, aging than as a treated/untreated test.

2. Materials and methods

2.1. The case study: the complex Cathedral-Baptistery in Pistoia

Figure 1. Cathedral of San Zeno and the bell tower.

Figure 2. Baptistery of San Giovanni in Corte in Pistoia

As has been said, this study aims to evaluate the residual efficacy of some water repellents used in the conservation of stone monuments, after a certain period from their application aiming to establish when a new one should be carried out to avoid the occurrence of stone degradation phenomena.

For this purpose, some stone monuments that had undergone conservative interventions in recent years needed to be chosen. The Cathedral of San Zeno, its bell tower, figure 1, and the Baptistery of San Giovanni in Corte in Pistoia, figure 2, suited the aim for several reasons: the same lithotypes, the same environmental conditions, the different state of preservation, the fair number of documented restorations performed at different times.

2.1.1. *Stones.* On-site tests were carried out on three different lithological types: white marble, serpentine, and gray sandstone. For each type of stone, significant slabs with known treatment and year of execution have been chosen. Each point was marked with a two-letter (AM = white marble tests, AS = serpentine tests, AA = gray sandstone tests) and two-digit progressive number code.

2.1.2. *Dating of conservative interventions.* The choice of the test points was made through a combined evaluation of past restorations information and of accessibility; the following restoration works were taken into consideration:

- no intervention (date 0) and then1999-2000 and 2000 for the cathedral, figure 3;
- 1997-2000 for the bell tower, figure 3;
- an overall restoration between 1999 and 2000 and several new interventions in subsequent years (2014, 2017, 2018) on the various fronts for the baptistery, as highlighted in figure 4.

Figure 3. Investigated points /areas per date of restorations on the cathedral and the bell tower.

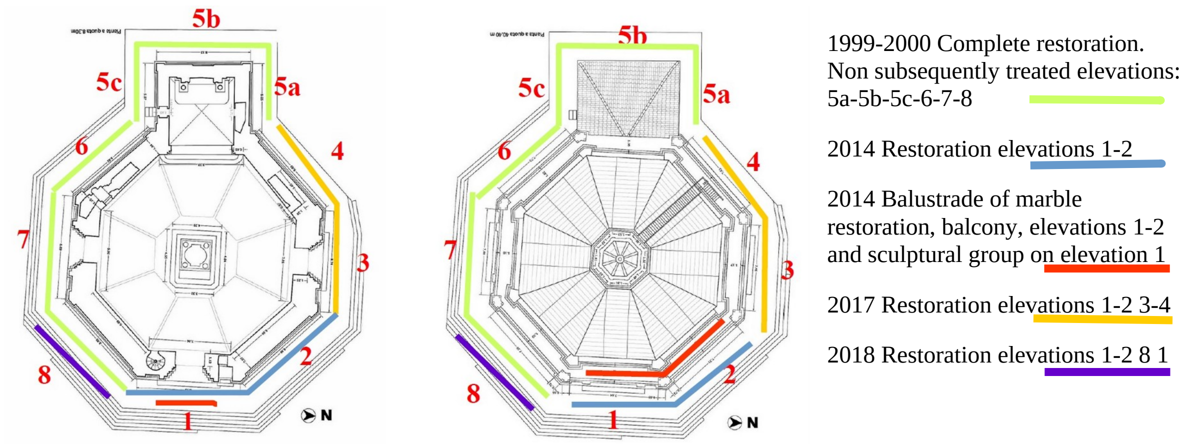

Figure 4. Dates of restorations of the baptistery.

2.1.3. *Water-Repellent treatments.*- White marbles (mainly Apuan marbles, but also some travertine, have been investigated), were all treated with siloxanes or polymethylsiloxanes (also some 'scialbi' were detected on many travertines of the bell tower and some last slabs of the baptistery);

- Serpentines were all treated with hexafluoropropene-vinylidene fluoride in the various formulations that it has had in the products since the late nineties of the last century to today;
- Gray sandstone was treated sometimes with ethyl silicate, sometimes with hexafluoropropene vinylidene fluoride, and sometimes with polymethylsiloxanes.

The framework of treatments on the different lithotypes of the two monumental complexes can be summarized as follows in table 1.

Table 1. Framework of treatments on the different lithotypes of the two monumental complexes.

SLAB	YEAR	IDENTIFIED PRODUCT	SLAB	YEAR	IDENTIFIED PRODUCT
AM1[1] - AM2[2] - AM3[1]	1999	'Scialbi'[3] and (dubious) S	AS1-AS2-AS3	1999	H
AM4 [2]	1999	S	AS5	2014	H
AM5-AM9 -AM10	2000	P	AS6-AS9	2000	H
AM6 – AS4 - AA4	0	'Scialbi'[3]	AS7	2017	Dubious: H or P

AM7-AM14	2014	P	AA1-AA2-	1999	Ethyl silicate
AM8	2000	‘Scialbi’[3] and P	AA5-AA9	2000	Ethyl silicate
AM11-AM12	2017	P [4]	AA6 - AS8	2017	H
AM13	2017	H	AA7-AA8	2014	P

[1] travertines; [2] column; [3] whitewash with lime milk; [4] after polymerization.

S = Siloxanes; P = Polymethylsiloxanes; H = Hexafluoropropene-vinylidene fluoride

Disclocation of the slabs:
- AM1, AM2, AM3, AM4, AS1, AS2, AA1, AA2: bell tower
- AM5, AM6, AS3, AS4, AA4: cathedral
- AM7, AM8, AM9, AM10, AM11, AM12, AM13, AM14, AS6, AS7, AS8, AS9,AA5, AA6, AA7, AA8, AA9: baptistery

2.1.4. *Method.* The contact sponge water absorption test (UNI 11432: 2011) [1] normally performed as treated/untreated test, in this study case, is rather used as a comparison test between treatments with different and known aging. The test was carried out on several slabs for each lithotype and treatment and by a single operator to avoid introducing any errors due to different manual skills. The amount of the absorbed water was as usual calculated using the following equation:

$$\text{Wa (g/cm}^2\text{ x min)} = \frac{Pi - Pf}{23{,}76 \cdot t}$$

Average of n° 3 measurement, where: t= contact time in minutes, Pi = initial weight in grams, Pf = final weight in grams, 23.76 = surface of the sponge in cm^2

The tests were all performed in just two days, in similar climatic conditions for temperature and relative humidity. A specific sponge has been designed for each lithological type. During the tests, the environmental data were also detected: ambient temperature, relative humidity, and slabs' contact temperature and humidity. Where possible, the extension of the sponge fingerprint on the stone and the time for drying was also detected. Moreover, some tests were performed as a validation of the whole test system (AM7, AS5) in order to estimate the influence of stone superficial grain size (AM7-AM14, AM3, AA5-AA9, AA7-AA8) or the presence of ‘Scialbi’, whitewash with lime milk, (AM6, AM1 AM2, AM3, AM8, AS4, AA4). These details, further information and the entire data set regarding the tests, the location of the slabs investigated, the environmental parameters, the absorption values, can be found in the doctoral thesis Martelli M [2].

The equipment used was composed as follows:

- Kit contact sponge (3 sponges and 3 polycarbonate contact plates), (CTS Srl, 2014);
- Precision digital scale (Homgeek TL-Series, with wind shielding system) capacity 50g, accuracy 0.001g, precision ± 0.001g;
- Trotec BC21 thermohygrometer: Air temperature range -30/100 ° C, accuracy 0.01 ° C, precision ± 1 ° C; Relative air humidity 0/100%, resolution 0.01%, precision at 25 ° C and 5-95% HR: 2%;
- Contact thermometer; - Contact humidity meter; - Stopwatch.

An example of performed measures per point is shown below in table 2.

Table 2. Example of performed measures of water absorption by contact sponge and environmental parameters; Point AM6, white marble, cathedral S-O, year 0.

Test	DP	TA	TC	HR	HRC%	t	Diam mm	Ta
1	0.064	29.5 °	28.2 °	43.1 °	1.3	3 '	6.1	3 '
2	0.055	29.5 °	28.2 °	43.1 °	1.3	3 '	6.1	3 '
3	0.063	29.5 °	28.2 °	43.1 °	1.3	3 '	6.6	3 '

	DP_1	Wa_1	DP_2	Wa_2	DP_3	Wa_3	DP_m	Wa_m
	0.064	0.89787	0.055	0.77160	0.063	0.88384	0.061	0.85110

3. Results and Discussion

Water absorption tests returned data ranging from 0.440 to 5.98 mg/cm² per minute on white marbles, from 0.744 to 4.938 mg/cm² per minute on serpentines and from 0.669 e 11.565 mg/cm² per minute on gray sandstone, as shown in the following graphs where amount of water absorbed (mg/cm² per minute) are plotted on the y-axis, while corresponding test points, year of treatment and exposure are plotted on the x-axis.

3.1 *General consideration - white marbles.* White marbles (figure 5), has been taken as a touchstone for the entire research. On them, the different responses due to stone superficial grain size or origin of the lithotypes have been tested, for example, AM7-AM14 and AM4-AM5 [2]. Given the big gap of the results, in the overall evaluation of the treatments, we, therefore, tried to select slabs that had similar characteristics (in particular grain size, state of conservation/decay) to have more reliable results in terms of effectiveness of the water-repellent treatment.

Figure 5. White marbles; detail of point AM14

The water absorption data show discrete differences between the slabs with treatments carried out in the year 2000 and those with the most recent treatments, except in the case of point AM7 (treatment year: 2014), a slab of poor quality and which appears very degraded (used in fact as system validation). However, interesting results derive from the comparison between absorption of the AM1-2-3-6-8 points, all with treatments ascribable to the years 1999 and 2000 and the absorption values of the AM14 point, 2014 treatment. Figure 8 shows how the absorptions detected in these elements are decidedly low compared to those of point AM14 (polysiloxane treatment, 2014), exception in the case of AM3 (travertine with large pores).

3.2 General consideration - serpentines. In this case (figure 9), the distribution of the highest absorption peaks appears more tied to the state of conservation of the surfaces than to the age of the treatment. In any case, the decidedly lower absorption is still that of the last treatment carried out in 2017 with Fluoline HY hexafluoropropene-vinylidene fluoride used as anti-writing in the base part of the Sides 3 and 4 prospectuses (point AS8, figure 6).

Figure 6. Serpentines; detail of point AS8.

3.3 *General consideration - gray sandstone.* Gray sandstones are the lithological type that showed the greatest excursion between the treated / untreated absorption data (figure 10), with considerable differences between the slabs with the oldest treatments (years 1999/2000) and those with the most recent treatments, figure 7. Two slabs were also identified to assess how much the surface grain of the stone could affect the extent of capillary absorption, points AA5 (figure 7) and AA9, with the same year of treatment, on which to compare the results. Finally, also in gray sandstone, the comparison between the water absorption of the whitewashed parts is interesting (even if in this case less significantly than for marble since no sandstone was found with bleaching outside), figure 10.

Figure 7. Gray sandstone; detail of point AA5

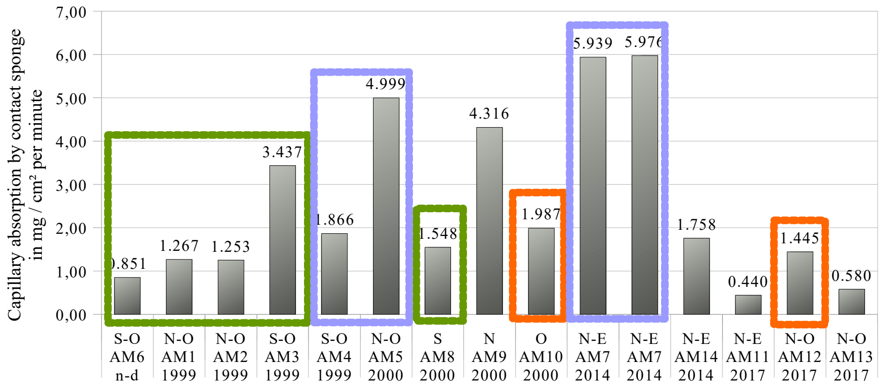

Figure 8. White marbles: boxed in green: slabs with whitewash; boxed in orange, tests on horizontal parts AM10, AM12 (not further considered); boxed in purple, AM7-AM14 and AM4-AM5, validation of the tests.

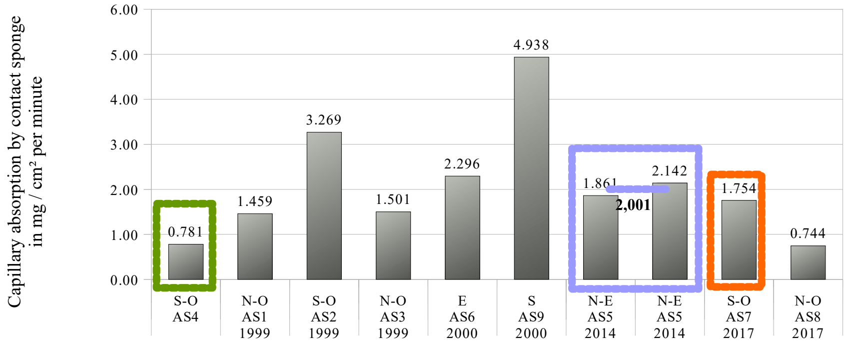

Figure 9. Serpentines: boxed in green: slabs with whitewash; boxed in orange, AS7 slab with dubious treatment; boxed in purple, AS5, validation of the tests.

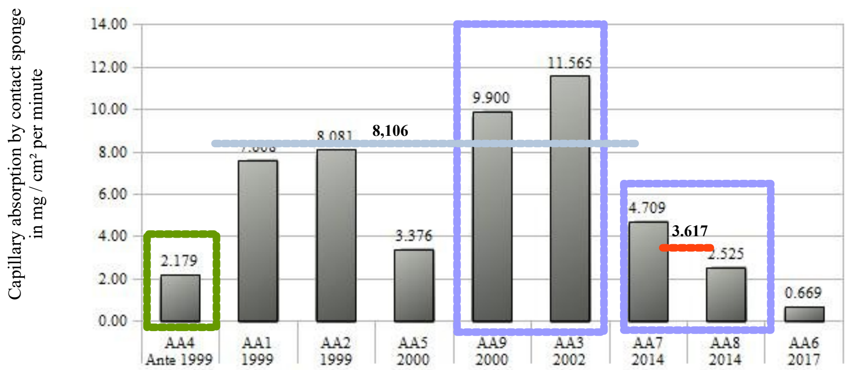

Figure 10. Gray sandstone: boxed in green: slabs with whitewash; boxed in purple: validation of the tests.

For the reasons expressed in the previous paragraphs and above (point 3), also illustrated on the graphs, the assessment of the residual effectiveness of treatments has been carried out considering the data of points:

- AM5-9(average 2000) – AM14(2014) – AM11(2017) – AM13(2018) for white marble,
- AS1-2-3-6-9(average2000) -AS5(2014) -AS7(2017) - AS8(2018) for serpentines,
- AA1-2-3-5-9(average 2000) -AA7-8(average 2014) -AA6(2017) for gray sandstone.

For all three lithotypes it is possible to read how the slabs with older water-repellent treatments (about 20 years), give back significantly higher absorption values than the slabs with most recent water-repellent treatments, 2014-2017; the data relating to the areas treated in these two years also differ significantly from each other.

The general overview of this data set can be summarized in Figure 11, which shows the absorption values of the three lithotypes grouped by 'year' of treatment, each with its own treatment (white marble: polymethylsiloxanes; serpentines: hexafluoropropene vinylidene fluoride; sandstones: polymethylsiloxanes and hexafluoropropene vinylidene fluoride); it can be noted how water absorption is strongly reduced by recent treatments on marble and sandstones, while a reduction is less appreciable on serpentines.

According to the literature (among others [3], [4], [5], [6], [7]), the effectiveness of water repellent treatments applied 18 years apart can be assumed equal to 0%. Thus, the absorption values of the various materials related to the treatments carried in the years 1999/2000, can be taken as treatment efficacy data equal to 0%. In analogy to the studies conducted [8] and [9], the following percentages of reduction of capillary water absorption values can be noted (table 3):

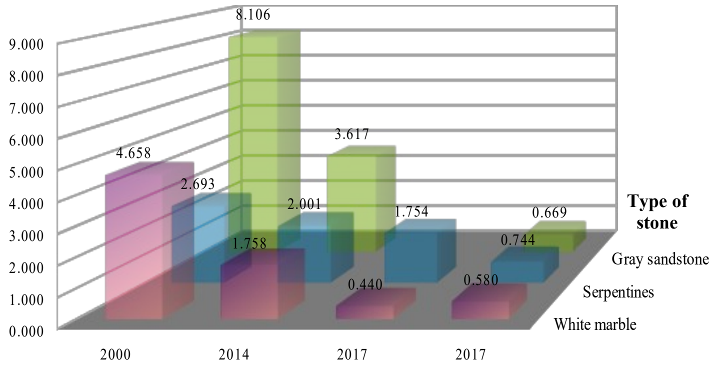

Figure 11. Capillary absorption by contact sponge in mg / cm² per minute; comparison of average 1999/2002, average 2014 and 2017 treatments.

Table 3: Water absorption values and reduction of the effectiveness of the water repellents.

	White marbles			Serpentines			Gray sandstone		
	18 years	4 years	1 year	18 years	4 years	1 year	18 years	4 years	1 year
WA	4.658	1.758	0.440	2.693	2.001	0.744	8.106	3.617	0.669
Efficacy	0.00%	65.04%	94.63%	0.00%	27.73%	78.19%	Efficacy	0.00%	56.78%

In table 3, the absorption values and the reduction of the effectiveness of the water repellents are put in relation to the individual lithological types. The table show decreases in treatment efficacy in four years (2017 treatment - 2014 treatment) of about 30% (29.58%) for white marble, over 50% (50.47%) for serpentines and about 38% (37.29%) for gray sandstones.

4. Conclusions

According to previous considerations, in the specific field of water-repellents, the main results of this research can be summarized as follows:

- siloxanes applied on marble and sandstone and fluorinated elastomers applied on serpentines have an immediate high water repellent power (one year after treatment) but a significantly lower degree of water repellency only after four years after treatment (- 30% for white marbles, - 50% for serpentines, - 38% for sandstones, from the comparison between the results of the respective 2017 treatments - 2014 treatments);

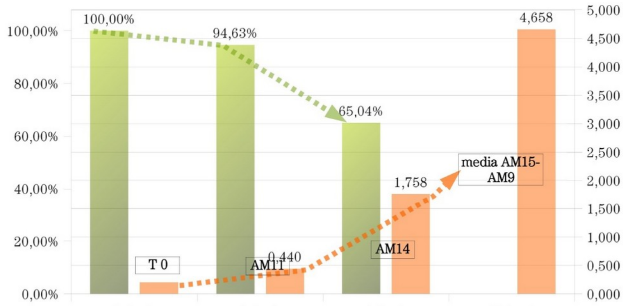

Figure 12: White marble, summary of the results:: water absorption values and reduction of the effectiveness of the water repellents

- the loss of effectiveness of the initial water repellency would mean that the stone should be re-treated after 2-3 years in order to guarantee high water repellency and adequate protection from the effects of pollution [4];

- the protection of stone surfaces with lime milk whitewashes seems more effective and stable over time compared to water-repellent treatments with synthetic polymers.

Given the lack of in situ monitoring, years after treatment, this research, trying to assess the residual efficacy of polysiloxanes and fluorinated elastomers on the observed lithotypes, brings a considerable contribution to the possibility of identifying the durability of traditional conservation treatments of stone.

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Moreover, the research could shortly provide further results. A monitoring slab (treated/untreated) for each of the three lithological types, has been left for further comparison. The data that will derive will complete the forecasting framework with a 'Time 0' of maximum efficacy; this will enable having a more reliable estimate of the drop of effectiveness over time (as represented in figure 12 regarding the data collected on white marble); water absorption could indeed be annually detected in the coming years to approximate a relatively reliable curve of decay for the specific conservation treatments studied.

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Author Contributions
M Martelli: Conception and design, collection and assembly of data, and data analysis and interpretation; M Martelli and T Salvatici: performing of experiments; M De Vita contributed support in conception and design and C A Garzonio contributed materials/analysis tools; M Martelli wrote the paper (excluded M De Vita's part), M De Vita wrote the first paragraph of the *Introduction*; T Salvatici: proofreading.

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