LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL

International Symposium
Stone Consolidation in Cultural Heritage

Full Papers

Editors: : José Delgado Rodrigues and Marluci Menezes

LNEC, Lisbon, 23-25 March, 2022

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Preface

The publication plan defined for the Stone Consolidation 2021 symposium provided for the publication of an extended abstract of each of the submitted communications and offered the possibility of submitting a full article for those who wanted a more detailed presentation of their research work.

The extended abstracts are published in paper format while full articles are included in this e-book. The electronic format allows for a less restrictive size for submitted texts and it is gratifying to see that the authors have used this offer to present and discuss their results and achievements extensively, and that they have made useful and important contributions to the progress of the research and to improve the practice of stone conservation.

Lisbon, March 2022

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Selection of a consolidant for the fixation of mineral pigments over the surface of the Tlaltecuhtli monolith

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SUMMARY: An important discovery in front of the main steps of the ruins of Templo Mayor, the major religious Aztec site in Mexico City, took place in October 2th, 2006. The archaeological works conducted by the Urban Archaeological Program, coordinated at that time by Alvaro Barrera, unearthed a massive sculptural relief which has been considered one of the most important findings in this area (López Luján, 2015:329). The archaeologists found a huge monolith depicting the earth goddess Tlaltecuhtli in this place. The complexity of this conservation challenge, needed to seek for the participation of different specialists. This multidisciplinary effort guided the work to a scientific research that looked for the understanding about the interaction between the different substances that could be used in the fixation process and the sculpture´s constitutive materials. Tlaltecuhtli´s conservation project ended in an acceptable result for the monolith´s conservation, as well as for the recommendations and the efforts for its suitable exhibition in Templo Mayor Museum.

KEY-WORDS: Tlaltecuhtli, andesite, mineral pigments, Templo Mayor archaeological site

1. INTRODUCTION

An important discovery in front of the main steps of the ruins of Templo Mayor, the major religious Aztec site in Mexico City, took place in October 2th, 2006. The archaeological works conducted by the *Urban Archaeological Program*, coordinated at that time by Alvaro Barrera, unearthed a massive sculptural relief which has been considered one of the most important findings in this area (López Luján, 2015:329). The archaeologists found a huge monolith depicting the earth goddess Tlaltecuhtli in this place.

The Tlaltecuhtli monolith is the largest painted monument to be discovered in Mexico City to date, and because of its dimensions, we can say that it is larger than the Coyolxauhqui monolith and the famous Sun or Calendar Stone (Lopez Luján, 2015:331).

Tlaltecuhtli is a goddess who appears in the myths as the venerated mother who gives birth to all creatures (plants, animals, human beings, the sun and the moon), as well as the monster who devours them when they die (López Luján, 2010:106). This unique sculpture was found broken into four pieces, and it was clear, since the moment of the discovery, that some of its original colours had been preserved, but were delicate and poorly adhered to the surface.

Once the fragments were unearthed, the immediate challenge for the conservation team was to work for the stabilization of the decorative layer located under the soil that covered the stone surface. The importance of this object and its unique state of preservation, leaded the conservators to consider what they thought could be the better option for its conservation, carefully weighing the possible results that could be obtained in the process.

The complexity of this conservation challenge, needed to seek for the participation of different specialists. This multidisciplinary effort guided the work to a scientific research that looked for the understanding about the interaction between the different substances that could be used in the fixation process and the sculpture´s constitutive materials. Tlaltecuhtli´s conservation project ended in an acceptable result for the monolith´s conservation, as well as for the recommendations and the efforts for its suitable exhibition in Templo Mayor Museum.

2. THE DISCOVERY OF TLALTECUHTLI MONOLITH

The finding of Tlaltecuhtli´s monumental sculpture in front of Templo Mayor Archaeological Site, confirmed the enormous importance of its location. The reason why the archaeological works had to be done in this spot, was because the government of Mexico City ordered the demolition of two buildings that had been damaged since the earthquake that occurred in the city in 1985. This decision raised great expectations among archaeologists because the location of the corner of Argentina and Guatemala streets, was exactly in front of the Great Temple (Lopez Luján, 2015:329).

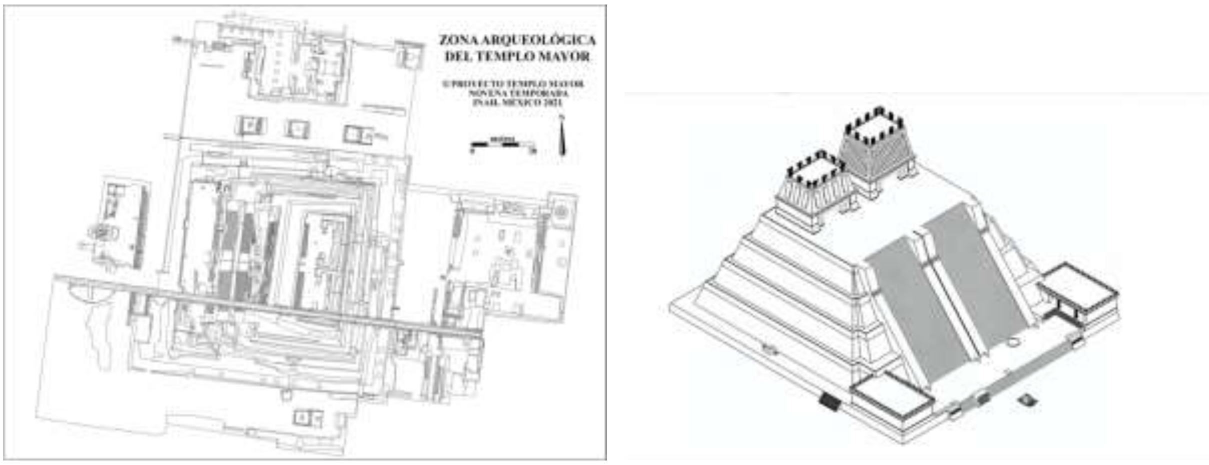


Figure 1. Tlaltecuhtli monolith in front of the archaeological site, located at the main steps of the Great Temple (Courtesy of PTM-INAH)

As a result of the demolition of these buildings, the Mexican government thought about the idea of constructing a new Cultural Center for the Arts of Indigenous Communities in the area. The goal changed completely when the previous archaeological works gave rise to the discovery of the massive sculpture of Tlaltecuhtli. The monumental monolith, which measures 4.17 x 3.62 x 0.38 m and weighs approximately 12.5 tonnes, is a one-eyed sculpture carved out in pink andesite. This sculpture, which was found broken into four pieces, shows the earth goddess Tlaltecuhtli with huge claws and a stream of blood going into her mouth. She squats as if she is giving birth and her face is flanked by large ears adorned with circular earrings. Her eyes are deep; her nose is wide and her hair is curled. Her teeth are revealed through an open mouth. Her elbows and knees are covered with skulls, and her four claws represent telluric beings (Barajas *et al*, 2009:2244).

Figure 2. Tlaltecuhtli monolith *in-situ* (PTM-INAH)

As expected, an archaeological finding of this magnitude caused the cancelation of the Cultural Center construction. Because of the importance of these facts, the Templo Mayor specialists guided their activities to an archaeological scientific research in order to initiate a new field season of the Templo Mayor Project in the area in which the monolith was found. Since March 2007 to date, a multidisciplinary working group, leaded by the archaeologist Leonardo López Luján, has been working in the exploration of this area (López Luján, 2015: 331). The specialists of Templo Mayor Project have been following meticulous scientific techniques and guiding their efforts in the understanding of the function and meaning of this important ritual area. Along fourteen years of archaeological research on this place, the archaeologists have found to date, 64 offerings related to the Tlaltecuhlti monolith, and from these offerings, they have recovered more than 60,000 different objects consisting in all kinds of gifts to the Aztec gods (López Luján, 2020: 17).

3. *IN SITU* PROCEDURES FOR THE MONOLITH´S STABILIZATION

Since the first moment of the discovery, the conservators were in charge of protecting the sculpture in order to see for its stabilization and conservation. The participation of the conservation team, which was leaded at that time by Virginia Pimentel, was really important and determined the good results for the constitutive materials of the monolith and its original colours.

During the liberation, the conservators focused in different procedures in order to avoid possible new damages that could be caused by the archaeological works that were taken around the sculpture. Because of the presence of high content of humidity that comes from the soil in Mexico City´s excavations, combined with the climate conditions that prevailed those days, the stone fragments were found almost completely saturated with water. The relative humidity around the stone presented an average of 70%. The team focussed then, to maintain these conditions without considerable variations (Barajas Rocha, 2019: 63).

The monolith was protected with different insulating materials to prevent rapid drying; there were also installed some tarps and wooden sheets to control the direct sunlight, as well as absorptive materials which were previously damped with water and carefully added over the stone fragments.

Figure 3. The controlled drying procedure with insulating materials (PTM-INAH)

Virginia Pimentel and her team were at all times, monitoring the surrounding conditions and looking for the security of the sculpture during this period. In this way, a slow and controlled drying process which took almost one year, contributed for the loss of humidity in the stone, taking place from the inside of each one of the fragments to its surface, and helping at the same time to prevent some possible effects such as salt crystallizations, cracking, spalling or losses.

Figure 4. Protection of the sculpture and its surroundings (PTM-INAH)

In November 2007 the stone was sufficiently dry to be lifted from its original place to the site street level in order to start working in the diagnosis and preliminary analyses of the monolith. The four fragments were removed from the ground by the contractor Luz Especializado, a specialized company that has more than 30 years of experience working in movements and transports of heavy and delicate objects. For this procedure, Luz Especializado used a long-armed massive crane, and as each one of the fragments was lifted, the crane placed them over temporary wooden support bases padded with foam, that were ready and waiting in the street. Once the fragments were stable over their temporary supports, a gatehouse and barrier for security were constructed around them, and since that day, this gatehouse was transformed in the new conservation laboratory for the Tlaltecuhtli monolith.

Figures 5, 6, 7 and 8. The lifting procedure for the four fragments from the site to the street level (PTM-INAH)

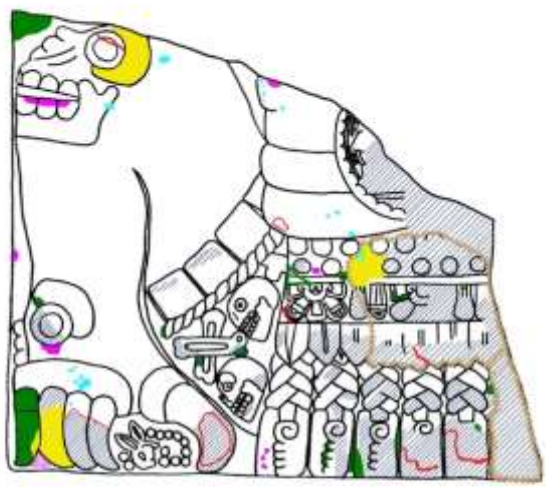
4. THE DIAGNOSIS AND THE CONSERVATION PROPOSAL

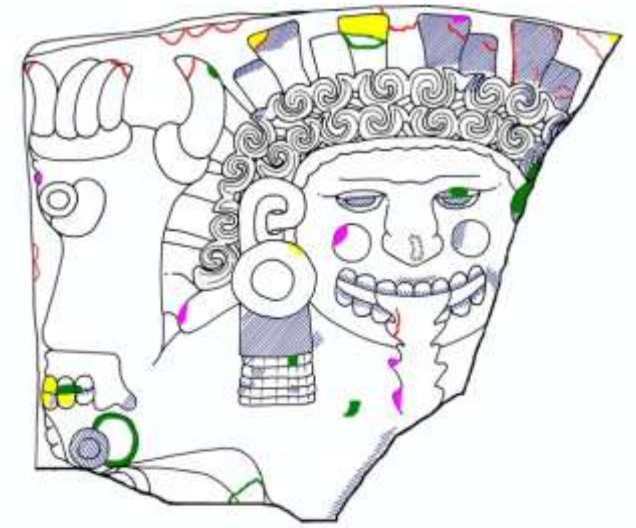
The second phase for Tlaltecuhtli´s conservation project started on June 2008. With the fragments already in the laboratory, we worked in a meticulous and detailed record which helped us in the understanding of the monolith´s precise state of conservation. The stone in which Tlaltecuhtli was carved, was identified by Jaime Torres Trejo (2008) as a lamprobolite andesite, composed mainly of aluminium, calcium, iron and magnesium. As a result of the observations we made to the sculpture, we could be able to identify and to catalogue each one of the alterations that were detected over the fragments. This diagnosis was based in direct observations over the constitutive materials of the monolith, and lended us to the conclusion that the lamprobolite andesite in which the sculpture was carved, was stable.

In addition to our observations, Torres detected in the samples the presence of ferromagnesian minerals with a healthy center. Also, the texture this samples had, let him stablish that the stone was in general, stable. Even though, in some cases Torres Trejo was also able to identify some oxidation in the ferromagnesian minerals (Torres Trejo, 2008:48).

Figure 9. Petrography image. Sample of the Tlaltecuhtli stone. Jaime Torres Trejo, 2008

As a result of this detailed diagnosis, we were able to detect some local alterations over the fragments. These alterations were caused either by the rituals that were taken place in the Aztec period, and also by the monolith´s interaction with the context after its burial (López Luján, 2010:111). The main alterations that could be detected were abrasion, cracklings, mineral and salt deposits, flakings, and also some missing parts. All the results derived from these observations were marked over graphics for each one of the fragments´ diagnosis.





Figures 20 and 11. Graphics obtained in the conservation diagnosis of each fragment (PTM-INAH)

As we were able to advance in this diagnosis, we parallelly worked in a cautious cleaning process that was focused in the removal of the dried soil that covered the original colours. We knew, since the moment of the discovery, that this massive sculpture conserved almost completely its decoration over its surface but at the same time it was really delicate because of the loss of the original binder. The mechanical cleaning process was carefully done with different tools such as soft brushes, needles and scalpels. This process took us around ten months to be concluded, and as a result of our detailed work, we could see for the first time, each one of the fragments showing a vivid original polychromy just as the Aztec people should have seen it (Barajas *et al*, 2016:19).


Figures 12 and 13. The cleaning procedure (PTM-INAH)

The skin of the goddess was painted in an ochre colour with a red background. She has curled dark red hair and her claws have bright white tips. The eyebrows of the skulls and the lines inside the circles of her cheeks, among other details, were painted in blue. On the goddess´s skirt there are skulls and crossed bones covered with white and painted with black designs.

Following full microscopic analysis of the polychrome stratums, we could also see that there was no plaster preparatory layer beneath the pigments. It seemed that the mineral pigments were mixed with the binder and then applied directly to the stone surface. The black was the only colour that was applied over the white colour and not directly to the stone.

Figure 34. Digital recreation of Tlaltecuhtli monolith obtained with 3D scan (Sugiyama, PTM-INAH)

Pigment samples were identified by Giacomo Chiari with X-Ray Diffraction analyses. He found that the red and ochre colours were iron oxides (hematite and goethite). In the case of the goddess´s hair, Chiari found the presence of hematite combined with a low percentage of a black mineral known as titanomagnetite (Chiari, 2008b). The blue pigment showed a high content of palygorskyte in combination with indigo, and therefore was identified as Aztec Maya blue. The dominant mineral used for the white pigment was calcite, and the black pigment assumed to be charcoal (Chiari, 2008a: 3-19).

Sample	Identified pigment	Chemical composition
White	Calcite	Calcium Carbonate $CaCO_3$
Blue	Aztec Maya blue	Palygorskite + indigo $(Mg, Al)_2Si_4O_{10}(OH)$-$4H_2O$ + indigo
Ocher	Goethite and some Hematite	Iron Oxyhydroxide + Ferric Oxide α $FeO(OH)$ + Fe_2O_3
Red	Hematite	Ferric Oxide Fe_2O_3
Dark red	Hematite y ligeras trazas de magnetita y cristobalita	Óxido férrico + Óxido ferroso-diférrico + Óxido de silicio Fe_2O_3 + Fe_3O_4 + SiO_2
Black	Charcoal	Carbon (not crystalline)

(Chiari, 2008a-b)

Even though, as we have said, the environmental conditions contributed to the loss of most of the original binding media, Chiari was also able to identify it by Gas Chromatography Mass Spectrometry. All the samples were tested for sugars, since plant gums such as copal or orchid mucilage were the suspected binding media. Although very little sugar was present, Chiari concluded the identification as an orchid mucilage containing glucose and mannose (Chiari, 2008a: 22).

Sample	Amino acids (Protein)	Fatty acids oil/wax/resin	Sugars (plant gum)
White	0.2% amino acids 0.95% glue 0.1% lipid	No oil, wax or resin	0.03% sugar (glucomannan/orquid)
Maya blue	Not tested	Not tested	<0.01% sugar
Ocher	0.2 % amino acids 0.95% glue 0.2% lipid	No oil, wax or resin	0.1% sugar (glucomannan/orquid)
Red with ocher	Not tested	Not tested	0.04% sugar (glucomannan, orchid)
White	0.1% amino acids 0.89 glue 0.1% lipid	No oil, wax or resin	0.02% de azúcares (glucomannan/orquid)
Red	Not tested	Not tested	0.01% sugar (glucomannan/orquid)
White	Not tested	Not tested	<0.01% sugar
Ocher	0.7% amino acids 0.95% glue 0.9% lipid	No oil, wax or resin	<0.01% sugar

(Joy Mazurek in Chiari, 2008a: 26)

We were able to see over the Tlaltecuhtli monolith a very well preserved decoration, that showed an almost complete coloured layer over the sculpture´s surface, and at the same time we knew that this polychromy was really delicate and unstable. At this moment and because of this situation, the Tlaltecuhtli monolith leaded us to work in a project that looked for its necessary stabilization and conservation. Obviously, this represented an important challenge for us as archaeological conservators, and the complexity of this challenge guided us to seek for the participation of different specialists (Barajas, 2012: 28).

We had the opportunity to work in a scientific research with the support and experience of Pedro Bosch Giral and Enrique Lima, from the Materials´ Research Institute– Universidad Nacional Autónoma de México. In this research, we decided to analyse a group of six different consolidating substances, and seek to the better understanding of the possible effects and results that could be obtained with each one of these options in combination with Tlaltecuhlti´s constitutive materials. This study looked to analyze the results for each one of the variables as well as their stability and their long-term behaviour.

5. ANALYSES AND RESEARCH

In March, 2009 we started to work in the planification of the activities and goals that were leading the research project for the fixation process. For us, it was meaningful to see that we were able to work in an analytical exercise which could bring us all the possible information that might contribute to the decision about an adequate conservation procedure. This experience brought us the opportunity to work in a multidisciplinary team for almost one year of research. This work promoted a series of optimal and collegiate discussion for the decision making in the preservation of the monumental sculpture (Barajas, 2012: 32).

The decision concerning on what consolidant could be used, guided this project. What we looked for, was to understand the different variables and the possible results to be obtained. Carefully weighing the options and cautiously approaching to the best outcome, some of the conservation materials that were commonly used in conservation and for stone preservation were selected, as well as some natural and more compatible products.

Considering also the final destiny that this sculpture could have, we finally selected and managed to evaluate six consolidating substances. The consolidants that were analyzed and studied were: Funori, Nopal exudate slobber, Methocel®, Klucel®, KSE 300® and Paraloid B72®.

Commonly used conservation material (for along 30 years)		
Name	**Characteristics**	**Preparation method**
Paraloid B72® (2.5% in Xilol)	Copolymer methyl ethyl methacrylate. This synthetic polymer has been used for different consevation purposes.	The polymer, inside a paper bag, is dissolved in the solvent at the needed concentration.
Compounds that are compatible with the original binding media		
Funori (1.25% in agua destilled water)	A seaweed- derived adhesive. It is primarily composed of Galactose and is similar to Agar. Natural polymer with low viscosity, tradicionally used by Japanese scroll mounters as a consolidant for friable media. (Swider and Smith, 2005:122).	Used in a low concentration in order to gain a better penetration. After hydrating the adhesive with destilled water, it can be prepared with the needed concentration.
Nopal Exudate Slubber 1:1	Arabinose, galactose, rhamnose and xylose are the monosaccharides present in the nopal exudates. This compound has been used for some conservation treatments.	The nopal, previously cleaned, is cutted in small pieces. Warm water is added until covering the nopal pieces. After 24 hours, the obtained mixture is sieved to extract the slobber, which is diluted with water.
Cellulosic compounds:		
Methocel® (Methylcellulose) 1% in distilled water	Methylcellulose: cellulose ether polymer. It is an excellent binder, film former and water-retention agent	A third part of the methylcellulose in water is heated at 80-90°C. The other two parts are cooled. The three parts are mixed together
Klucel® 1% in distilled water	Hidroxypropyl cellulose obtained from alkaline cellulose	It is prepared the same way as the Methocel. It can be disolved in ethanol, water or acetone/water 9:1.
Compounds that are compatible with the Stone:		
KSE 300E® 1:1	Solvent-free stone strengthener on a silicic acid ester base. Produced by Remmes, Germany. It reacts with the relative humidity and with humidity from the inside of the stone. The Silicon Dioxide (SiO_2) bonds with the stone particles, working as a consolidant.	Disolved in ethanol 1:1

Original fragments of the stone were found right beneath the center of the sculpture. Assuming that these fragments possibly belong to the monolith, we selected small samples of this andesite stone. All of the samples were painted in ochre pigment using a brush, and this pigment was fixed to the stone surfaces with each one of the selected different substances. We also worked with a painted sample without consolidant for comparison purposes.

We worked with two groups of samples treated with each one of the selected substances as well as a painted sample without treatment. One of this group of samples was treated to simulate ageing. For this procedure, the samples were placed in an accelerated ageing chamber to simulate the deterioration after time under specific conditions of humidity and solar irradiation. Temperature was maintained at 45-50°C for 16 hours under UV exposition and a relative humidity of 20-30%, and then 8 hours at 45-50°C under 80-100% of relative humidity without UV exposure. This cycle was repeated for 75 days which were equivalent to 3 years in real time. The purpose of this treatment was to determine how much the fixation agents could modify the pigments and/or resist the action of time. At the same time and because of this purpose, we decided to also analyse a group of "fresh samples" that wasn't treated in the accelerated ageing chamber. This method gave us the possibility to compare the different analyses results between the aged and the fresh samples (Barajas *et al*, 2010: 2882).

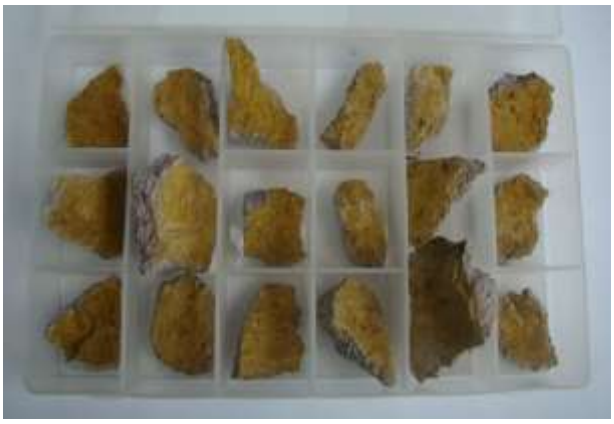


Figure 45. Samples ready for the analyses

Figure 56. Accelerated ageing chamber

The aged as well as the fresh samples, were studied by powder X-ray Diffraction (XRD) to identify the different compounds. The morphology of the different surfaces on each one of the samples was also studied with Scanning Electron Microscopy (SEM), as well as some elemental analyses in selected zones of the samples with an EDX (Energy Dispersive X-ray) spectroscopy. We also managed to do some leaching tests over the samples, by softly rubbing humidified cotton against the surface of the different samples in order to measure the effectiveness of the fixation process. Finally, an analysis by Nitrogen Adsorption (BET) contributed to calculate the surface area and pore diameter values for each one of the samples. Surface areas were calculated with the BET equation and the pore diameter values with the BJH method (Barajas *et al*, 2009: 2883).

By this analytical work, we were looking forward to understand about the composition and the morphology of the film that would be formed in the stone surface after the fixation process, and also to evaluate the chemical and physical interaction between the stone, the original colours and the consolidating substance. We also seeked to understand the variances between the surfaces before and after the different fixative applications. Considering the possibility of exhibiting the Tlaltecuhtli monolith on its original place, we were also really concerned about the assessment of the andesite´s porous system after the consolidation treatment. This was because, as we have said, the site conditions present a variable content of humidity which depends on the climate conditions and the subsoil of our city. Therefore, we were looking forward to maintain a natural porous system in the stone even after the consolidation process. This could contribute to gain a natural humidity exchange from and inside the sculpture after the treatment.

Searching for a compound that could generate a superficial film without completely sealing the natural porosity of the stone, we managed to compare this characteristic between the consolidated samples (before and after the accelerated ageing) and the sample without treatment. The comparisons between each one of these samples before and after ageing, helped us to understand some of the results: we didn´t observe significant differences in the XRD patterns after ageing for the samples treated with Paraloid B72® and with Methocel®. Other consolidants, however, evolved as the ageing process went on. The peaks due to Goethite, that could be seen in the sample treated with Funori® became more intense, suggesting a sintering of the pigment crystals after time. On the contrary, for the Nopal slobber we could see that after time, the peaks turned out to be less resolved, assuming a possible dissolution of the hydroxide in the slobber. We could also confirm that the KSE 300® induced the formation of small quartz particles. This crystalline phase was present in the XRD pattern of the fresh sample treated with KSE 300®, but peaks due to quartz vanished after ageing, suggesting a possible redistribution of this phase.

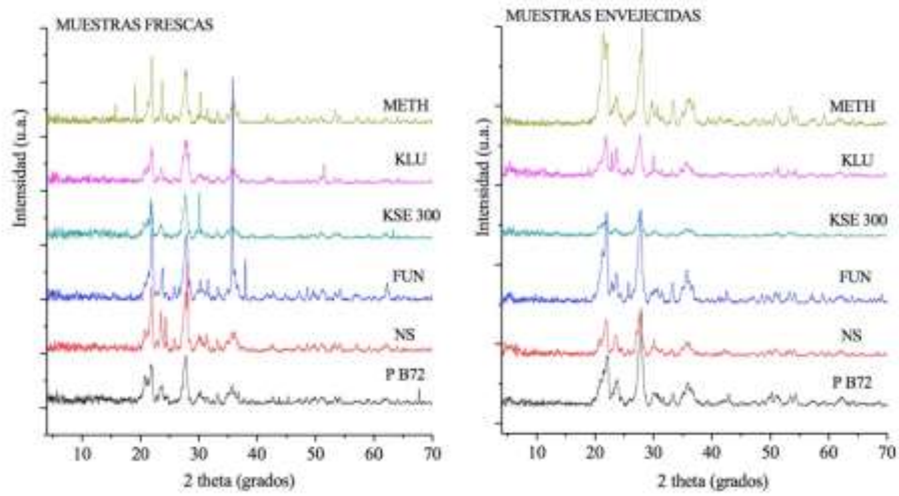


Figure 67. XRD patterns for the six different options

At this moment of the research, we needed to select the possible substances that could be applied for the fixation process. The leaching tests helped us to understand if each one of these substances was really successful. This could be corroborated when the humidified cotton was completely clean after carefully rubbing it over each one of the samples. After doing so, we saw that Paraloid B 72® and KSE 300® were completely effective. At the same time, we saw that Funori® and Klucel® contributed to a partial fixation of the pigment. These results guided us to the decision of continuing our studies just for Paraloid B72® and for KSE 300®, by carefully evaluating and discussing all the results we have obtained.

Leaching tests results		
Fixative	**Cotton**	**Results**
Paraloid B72® (2.5% in Xilol)	It didn´t have pigment	100% effectiveness
Nopal exudate	It had pigment	Not effective
Funori (1.25% in distilled water)	A small quantity of pigment	We should try more applications before any conclusion
KSE 300® 1:1 in Ethanol	It didn´t have pigment	100% effectiveness
Klucel® (1% in distilled water)	A small quantity of pigment	We should try more applications before any conclusion
Methocel® (1% in distilled water)	It had pigment	Not effective

Results and discussion

Even though, the decision after the leaching tests guided us to select the Paraloid B72® and the KSE 300®, we managed to do all the analyses for the six consolidating substances. We consider that the results obtained in this research can contribute to evaluate different options in future cases. Even though we have in our records the complete results and discussions for the six consolidating substances, in the next lines there are only presented the SEM and the Nitrogen Adsorption analyses results for the Paraloid B72® and the KSE 300®.

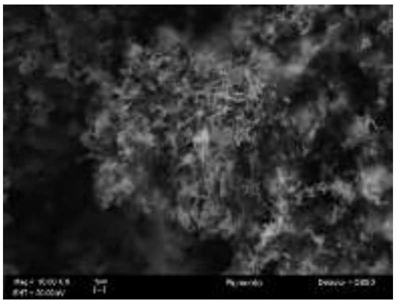
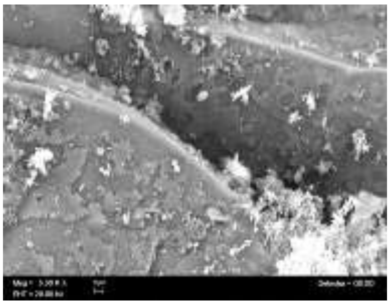
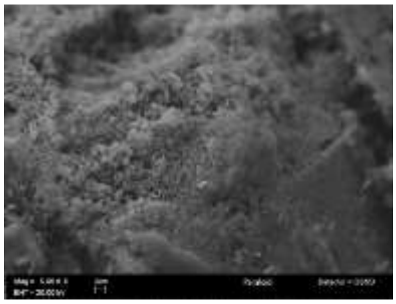




Figure 78. Non treated sample Figure 89. Paraloid B72® Figure 20. Paraloid B72® after ageing

The SEM images obtained for the samples treated with KSE 300® and with Paraloid B72® showed that, for the fresh samples these two consolidants appear to be covering the painted stone surface in a different way: comparing the images with the one obtained for the sample without any treatment (just the pigment over the stone surface) we found that in the sample treated with Paraloid B72®, the andesite was completely covered by a polymer which formed a smooth surface in combination with the pigment´s particles. KSE 300® also covered the andesite surface, but globular particles were formed, and the surface did not turn out to be fully sealed.

After ageing, the compact layer that was initially formed in the sample with KSE 300®, seemed to be less uniform and less compact because, as we could see in the diffractions, quartz was formed. We could then conclude that, as a consequence of quartz formation, the surface of the aged sample treated with KSE 300® did not seem completely sealed, and that some free spaces were remaining.

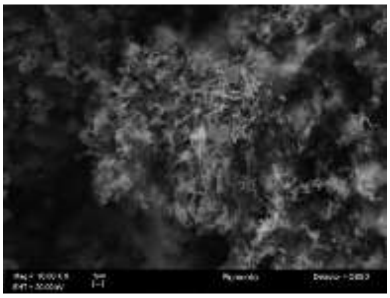
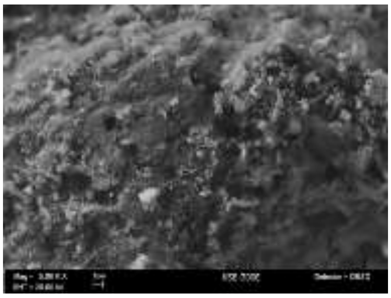
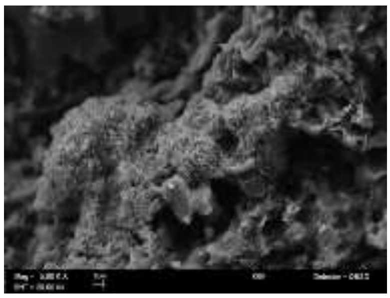




Figure 21. Non treated sample Figure 22. KSE 300® Figure 23. KSE300® after ageing

Evaluating and comparing the results obtained in the XRD and the SEM analyses for these two consolidants, we could conclude that Paraloid B72® does not induce changes regarding crystalline composition, however, it was clear in the SEM images that Paraloid B72® sealed completely the porosity in the stone´s sample. As for the KSE 300®, we noted in the XRD that it modifies the composition because of the formation of quartz crystals from the silicic acid, but the SEM images showed that the surface of the aged sample treated with this consolidant was not completely sealed; therefore, we knew that KSE 300® induced a more permeable surface than Paraloid B72®.

Considering these results, obtained from the XRD and MEB analyses for this two consolidants, we thought that it would be important to obtain a better understanding about the porosity and future permeability that could be gained in the stone´s surface after the treatment. Therefore, the possibility of analysing the samples treated with Paraloid B72® and with KSE 300® by Nitrogen Adsorption (BET) and to calculate the surface area and pore diameter values, was really helpful.

In the Nitrogen Adsorption analysis, we compared the values obtained for the samples treated with Paraloid B72® and with KSE 300® with the sample without consolidation treatment. The specific surface area of the non-treated sample, as determined by BET equation, was 20.7 m^2/g and the average pore diameter was 122 Å. The values obtained for the sample treated with Paraloid B72® showed that the surface was sealed and that the access to pores was inhibited. This was clear because the specific surface area was reduced to 10.0 m^2/g. Still, after ageing, surface treated with Paraloid B72® was not accessible to molecules as small as nitrogen. The pores that were formed resulted bigger than in the non-treated sample, because there were only the macropores that were generated between the agglomerates (Specific surface area: 10.8 m^2/g, and pore diameter: 247 Å).

The KSE 300® induced an opposite behaviour: the specific surface area in the samples increased as a consequence of the deposition of small particles of quartz into the andesite´s macropores. Even after ageing, we could see that the surface in the samples treated with KSE 300® was accessible to nitrogen molecules (Specific surface area: 23.3 m^2/g and pore diameter 172 Å). With the values obtained in the samples treated with KSE 300® we could conclude that, if the monolith was going to be treated with this consolidant, its surface surely would be permeable to air and to water.

Sample	$A^{\dagger}$, $m^2 \cdot g^{-1}$	$d^{\dagger\dagger}$, Å
Andesite + pigment	20.7	122
Paraloid B72®	10.0	324
Aged Paraloid B72®	10.8	247
KSE 300®	21.2	125
Aged KSE 300®	23.3	172

† Surface area (BET method) †† Average pore diameter (BJH method)

All of the results guided the multidisciplinary discussions and the decisions for what we thought could be the more suitable treatment. With solid bases that contributed to sustain our proposal, we concluded that KSE 300® was chemically and physically compatible with the monolith´s original materials. We could also understand about the reactions that were going to take place between the stone, the pigments and the consolidant agent in short and in long terms.

With the application of KSE 300® to the stone´s surface, the decoration layer could be bonded, gaining stability by the formation of a microporous layer that would not seal completely the stone´s surface. This characteristic could contribute for a free humidity exchange from and inside the stone.

6. THE MONOLITH´S STABILIZATION AND ITS EXHIBITION

It´s known that KSE 300® reacts with the humidity from the environment or from inside the stone. In this process, the amorphous silicon dioxide bonds with the stone´s components; and the time this reaction needs to take place is related with the surrounding temperature and humidity. The reaction between the KSE 300® and the monolith´s fragments took approximately three weeks (Barajas, 2019: 149).

For this reason, we studied the conditions we had in the conservation laboratory at that time. As a result of this monitoring, we stablished to work in the application of KSE 300® with an average relative humidity of 40-50%. Therefore, the process had to be done before the rainy season in Mexico City, inside the laboratory with the doors and the windows closed.

The fixation process for Tlaltecuhtli´s decoration

In the process, important security procedures such as the use of gloves, masks and protection glasses had to be considered. This helped us to control possible damages that could be caused by the consolidation agent. The KSE 300® was prepared 1:1 in ethanol, and was applied to the stone by atomization. This method contributed to stabilize the superficial decoration with the stone, avoiding at the same time a deeper penetration, and therefore gaining a controlled fixation action.

The first application took place in January, 2010. Knowing that there were needed 2 to 3 weeks for the reaction to take place, we managed to execute four different applications inside the conservation laboratory. These applications were done over each one of the fragments, monitoring at all times the reaction and the evident results.

Figure 24. Application of KSE 300® over each one the fragments (PTM-INAH)

The last application of KSE 300® inside the conservation laboratory took place on April 19th, 2010. At this moment, the pigments were much more stable within the stone´s surface. Because of the chemical composition of the white, blue and black colours, in combination with the decoration technique identified for this unique sculpture, we decided to reinforce the procedure with KSE 300® using a complementary treatment.

For the white colour (calcium carbonate) we managed to apply calcium hydroxide also by atomization. These applications were done two times a week during all the time of the consolidation treatment. Considering the decoration technique, in which the black colour was always applied over the calcium white, we decided to use the same treatment for the black as for the white colour. In both cases, we could confirm the effectiveness of the calcium hydroxide applications.

It´s well known that the Maya blue is really stable, however, it presented some local damages such as detachments and flakings. In these cases, we managed to work on a process that contributed to re attach the small flakes, by carefully applying a synthetic adhesive (Mowithal B60H®). With this procedure, the blue colour gained a suitable stability.

Figure 25. Detail of the monolith´s decoration (Jesus Eduardo López, PTM-INAH)

The monolith´s exhibition in Templo Mayor Museum

At the beginning of 2010, the specialists in Templo Mayor Museum were working in the planification of a temporary exhibition about Moctezuma II (López Luján and McEwan, 2010). During the planification of this exhibition and considering that the fragments were already stable, we thought about the possibility of exhibiting the Tlaltecuhtli monolith to the public for the first time.

The curators and specialists of Templo Mayor Musem thought that this was a good idea, and the proposal for Tlaltecuhtli´s exhibition in the upcoming temporary exhibition guided the team in the specific proposal for its transportation from the site to the museum, which is located just a few blocks away. After weeks of planning and discussing between different working teams, the fragments were finally taken from the site to the museum entrance. This procedure, which took us more than 18 continuous hours, was done with the participation of different specialists from INAH as well as with the help of Cordoba Plaza Company, which specializes in the packing and transportation of all kinds of museum objects.

The four fragments, already packed and prepared, were taken over a special truck with a crane, directly to the Templo Mayor Museum. This exhibition project provided the opportunity of showing Tlaltecuhtli´s monumental sculpture for the first time in one of the main areas, located in the museum´s vestibule. In this exhibition place, the four fragments were cautiously placed and joined one to each other. After hours of delicate working, we were able to see the unique and impressive image of the earth goddess showing its vivid polychromy in her new exhibition place.


Figure 26 and 27. Transportation and mounting jobs for Tlaltecuhtli´s exhibition (PTM-INAH)

Since 2010, the monolith shows to thousands of visitors its deep reliefs and its brilliant colours. With this objective, and concerned about the optimal monolith´s preservation during its exhibition inside the Templo Mayor Museum, we defined important recommendations that have been considered to assure its optimal long-term preservation.

The average relative humidity in the exhibition room is 50%. This condition should not vary from more than ±5% in one day. Since the temperature variations are intimately related with the relative humidity, we also seeked for the exhibition temperature conditions: the exhibition room presents an average between 10 – 25/28°C.

Also, we worked in the recommendations of an adecuate lighting system, and looked for a rank that should not overpass 50 luxes: led lightings with UV and IR filters were carefully installed around the goddess (Barajas Rocha, 2019: 191-207)

Figure 28. The Tlaltecuhtli monolith in the Templo Mayor Museum (INAH)

Ten years have passed...

After ten years of Tlaltecuhtli monolith´s exhibition inside the Templo Mayor Museum, we can be sure that this unique sculpture is one of the most visited objects. It can even be said that Tlaltecuhtli has converted in an iconic piece along the curatorial discourses in the museum. After all these years, we as conservators can be aware that Tlaltecuhtli´s decoration has been well preserved; and as part of the conservation and preservation activities, the museum professionals dedicate some of their actions working in periodically superficial cleaning procedures as well as monitoring and maintaining this monumental sculpture on its exhibition area.

Even though, we are at the same time aware about the necessity of focusing in future discussions which can guide to some decisions concerning about a plan addressed to some analyses and studies for the stone and its decoration. This plan will contribute to a better understanding of the interaction between the monolith´s constitutive materials and the consolidating substances after these ten years.

In this way, the future studies would contribute to evaluate the behaviour of our intervention in a long-term period, considering that the sculpture has been in a controlled atmosphere. It will also assist to define a necessary and adecuate procedure for a needed chemical cleaning process on the Tlaltecuhtli´s decoration.

After all these years we can be sure that the experience within the project for Tlaltecuhlti monolith conservation and exhibition, emphasizes the importance of working among different professionals and specialists who can contribute in the discussions leading to what could be considered the best decision for a conservation procedure and for an exhibition planification.

The analyses and studies that were executed as part of this project to sustain our decisions, helped us to focus our job in specific treatments and actions highlighting the importance of this kind of previous assessments. During the development of the project, the discussions between archaeologists, conservators, geologists, architects, physicals and engineers that participated in this experience, were essential to define the different results that lended us to take the final decisions.

Also, we think that this experience can contribute to stablish and define some new research themes concerning to similar problems that can be solved with the different substances that were analysed as part of this research.

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Multi-analytical assessment of the impact of curing conditions on the consolidation of selected sandstones by ethyl silicate

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SUMMARY: The long-term interaction of sandstone built heritage with outdoor and sometimes highly polluted environments is a major cause of decay, ultimately leading to significant loss of material. Ethyl silicate-based treatments have been extensively used in sandstone consolidation because of their chemical affinity to the substrates and stability. Among the main factors affecting the efficacy of the consolidation results, the application method and the curing conditions both play a significant role. In the present work, the effect of curing conditions on the consolidation of two sandstones with ethyl silicate is investigated by means of an integrated methodology combining laboratory and field-based techniques. Samples of Locharbriggs and Prague (Mšené) sandstone were treated by capillarity with a commercial ethyl silicate (Conservare OH, ProSoCo). Two different relative humidity (RH) regimes were selected for curing at 20°C: 50% RH, representative of reference curing conditions as recommended by the supplier, and 75% RH, representative of possible real application conditions in humid outdoor environments where controlled curing cannot be provided. The consolidation effects in both conditions have been evaluated and monitored using a multi-analytical investigation protocol. The strength increase was much more limited when curing was conducted at 75% RH, particularly for Locharbriggs.

KEY-WORDS: sandstone consolidation; ethyl silicate; curing conditions; DRMS; mechanical properties

1. INTRODUCTION

The long-term interaction of sandstone built heritage with outdoor and often highly polluted environments is recognized as a significant cause of decay (Přikryl and Smith 2007; Siegesmund and Snethlage 2014). The combined action of chemical and physical mechanisms can progressively impair the integrity of the mineral matrixes. Crumbling, granular disintegration, and powdering (ICOMOS-ISCS 2008) are the typical deterioration patterns observed in such conditions and can ultimately result in significant loss of material from the exposed substrates. Therefore, the consolidation of weathered sandstone surfaces is a relatively common yet still challenging phase of the overall preservation activity. To this end, ethyl silicate-based treatments have been extensively used in stone conservation (Wheeler 2005) because of their chemical affinity to sandstone substrates, particularly in the case of eminently silicate mineralogy, their generally better long-term stability compared to most organic resins, and despite their well-known tendency to shrinkage and crack, due to the capillary pressure developed during the xerogel formation (Scherer et al. 1996).

Several factors contribute to the final consolidation result, which ultimately arises from the complex interplay between the inherent substrate properties (in particular, mineralogy and microstructural features), the specific characteristics of the treatment material, the amount of applied product, the application methodology, and the curing regime (Pinto and Rodrigues 2008). Ethyl silicate develops a consolidation effect thanks to its reactivity in the presence of water. The hydrolysis of the initial silane groups leads to the formation of intermediate silanol species and the final development of siloxane bonds due to condensation reactions (Wheeler 2005). Therefore, the curing conditions to which the substrates treated with ethyl silicate are subjected during such reactions are critical to the final strength development (Franzoni, Graziani, and Sassoni 2015).

In the present work, the impact of two different curing conditions on the consolidation of selected sandstones with a commercial ethyl silicate is investigated through a multi-analytical assessment methodology. Samples of Locharbriggs sandstone (Scotland, UK), a medium-grained, silica-cemented sandstone with quartz and low amount of expanding clay, and Prague (Czech Republic) sandstone, a fine-to-medium grained, silica-cemented sandstone with non-expanding clays were treated by capillarity with a commercial consolidant (Conservare OH, ProSoCo), which consists of tetraethoxysilane monomer and dimer (Grissom 1999). Two different relative humidity (RH) regimes were selected for the curing at 20°C: 50% RH, representative of the reference curing conditions recommended by the supplier, and 75% RH, representative of possible real application conditions in humid outdoor environments where controlled curing cannot be provided. The consolidation effects in both conditions have been monitored for up to 4 months of curing time.

A multi-analytical laboratory protocol has been followed to characterize the distribution, penetration depth, and interaction between the consolidant and the sandstone substrates. The evolution of the silica gel has been monitored by FTIR spectroscopy in ATR mode on microscopy glass slides to assess the rate and extent of the polymerization. The final increase of mechanical cohesion is a crucial factor for the evaluation of the consolidation treatment and was performed integrating the results of laboratory testing of flexural- tensile strength with a field-based method (drilling resistance measurements).

2. MATERIALS AND METHODS

Stone substrates

The investigated substrates are Locharbriggs and Prague (Msěné) sandstones. Locharbriggs was selected as a medium porosity substrate with expanding clay, Prague sandstone as a medium-high porosity substrate with significantly lower mechanical strength, therefore deemed suitable to simulate a weathered substrate (Remzova et al. 2016). The main mineralogical and microstructural characteristics of the two stones are summarized in Table 1.

Table 1 – Photographic documentation and summary of the main features of the tested substrates

	Locharbriggs (LB) is a red Permian sandstone quarried in Southern Scotland, UK. Sub-rounded quartz grains constitute the main mineralogical phase, with minor feldspar, iron oxides, and clay. The clay content includes smectite and kaolinite (Graham 2016). The tested specimens have a medium grain size with well-defined bedding planes. The average porosity is around 20%, with a unimodal distribution centered at 11 μm.
	Prague (PS) is a white-light grey psammitic rock (Remzova et al. 2016) extracted from the Mšené-lázně quarry (Czech Republic). Quartz is the main mineralogical phase, with muscovite and feldspar as accessory minerals. Minor non-expanding clay, including kaolinite, is also present. The tested specimens have a fine to medium grain size, with sub-rounded quartz crystals, and show no evident bedding. The average porosity is 26-30%, with a unimodal distribution centered at 25 μm.

Specimen preparation

50 mm cubic specimens of each stone were prepared by wet cutting using a tile saw. Specimens were washed in deionized water after cutting, dried at 60 °C until constant mass, and conditioned at room T and RH before consolidation. At least five cubic specimens were prepared for each stone and curing condition.

Flexural and compressive stress tests were conducted on 25 mm x 25 mm x 110 mm Locharbriggs and Prague sandstone prisms (same sample preparation as above). LB specimens were cut in a way that the bedding was parallel to the major dimension of the specimen. Ten prismatic specimens were prepared for each stone and curing condition.

Consolidation treatment

The consolidation treatment was performed using a commercial ethyl silicate (Conservare OH, Prosoco®). The concentration of active ingredients is not provided. The safety data sheet reports the presence of dibutyltin dilaurate, thus indicating that the product is a catalyzed ethoxy silane.

The treatment was applied by capillary absorption at room conditions (50% RH, 20 °C). A stainless steel mesh was placed underneath the specimens, allowing for full contact of the absorption faces with the liquid consolidant up to 3 mm depth. The treatment was conducted until full saturation. The absorption face for treating LB specimens was perpendicular to the bedding.

Two curing conditions were selected to investigate the influence of reference versus higher humidity conditions on the strength development:

- 50% RH – 20 °C, obtained by storing the specimens in controlled lab conditions (considered reference condition);
- 75% RH – 20 °C, achieved by storing the specimens in sealed containers with a saturated NaCl solution (humid condition representative of humid climates and/or humid real application conditions).

The curing conditions were continuously monitored and recorded using temperature/relative humidity data loggers (Hobo, Onset®).

Thin layers of the commercial ethyl silicate were also prepared by applying the liquid consolidant on glass microscope slides to investigate the rate of formation of the silica gel in the two curing conditions. The slides were cured following the same curing protocol as the stone specimens.

Amount of absorbed product

The amount of product absorbed was quantified by recording the mass of the specimens before and immediately after treatment. The amount is expressed as the weight (g) of consolidant absorbed per 100g of the specimen. The final amount of absorbed consolidant (g/100g) is 6.6 (±0.1) for LB and 13.0 (±0.1) for PS. On average, the final absorption of PS can be approximated as twice the value for LB. The absorption behavior is consistent with the overall porosimetric differences between the substrates, considering the +37% porosity of PS with respect to LB before treatment.

Characterization methodologies

Compositional characterization

FTIR analyses of the consolidant over time during curing under the two RH conditions were performed with a Hyperion 3000 FT–IR microscope (Bruker Optics, Inc.) in ATR configuration. The consolidant was applied on microscopy glass slides. Spectra were acquired in the spectral range 4000-600 cm^{-1} with a 4 cm^{-1} resolution and elaborated with Omnic software for baseline correction and normalization. Analyses were conducted on the fresh material and after 3, 15, 30, and 60 days of curing.

Mechanical testing

Dynamic elastic moduli ($E_{dynamic}$) of the specimens before and after treatment with ethyl silicate (after 28 days and 120 days curing) were obtained by the ultrasonic pulse velocity method (ASTM C 597 and EN 12504-4) using Geotron UKS-D. The direct transmission technique was implemented using two UPE-D point-tip transducers, pressed at the center of the opposite square ends of the beams. The frequency and voltage used for both stones were 10 MHz and 200 mV, respectively.

The three-point flexural-tensile strength test was performed using an Instron 5885H universal mechanical testing machine. Specimens were loaded at a 1 kN/min rate. The span between the supports was 60 mm. The specimens were loaded so that the crack development was perpendicular to the bedding (LB). The flexural-tensile strength, σ_f, was calculated in MPa as:

$$\sigma_f = \frac{1.5 \times F_t \times L}{b^3}$$

where, Ft is the load at failure (N), L is the span between the supports (mm), and b is the side of the square cross-section of the prism (mm).

Test were conducted after 4 weeks (28 days) and 3 months curing (120 days).

Drilling resistance

Drilling resistance measurements (DRMS) were employed to evaluate the mechanical cohesion variation resulting from the treatment. The equipment used is a DRMS System by SINT Technology, equipped with a calibrated 100 N load cell. At least 3 measurements were carried out on each stone and curing conditions (after 120 days curing for the consolidated specimens). Measurements on LB were conducted along a drilling direction perpendicular to the bedding.

The measurements were conducted in standard acquisition mode, applying a moving average filter and 0.001 mm decimation. The correction of the wear effect was conducted on reference specimens of the same stone under evaluation, according to (Rodrigues and Costa 2004).

The final measurement conditions for the reference and treated specimens were:

- LB / 5 mm drill bit, 150 rpm rotational speed, 20 mm/min penetration rate, and 20 mm drilling depth
- PS / 5mm drill bit, 100 rpm rotational speed, 25 mm/min penetration rate, and 20 mm drilling depth

The average DR values were calculated on at least 3 measurements in the 1-18 mm depth interval after data correction for the wear effect.

Microstructural investigation

Thin sections from reference untreated stone and after consolidation (LB and PS) were vacuum impregnated and prepared with blue epoxy resin and polished. SEM-EDS analyses were performed with a Zeiss GeminiSEM 300 coupled to an Oxford Aztec EDS system. SEM images were collected using a back-scattered detector. The penetration of the consolidant within the pore network was qualitatively assessed by image analysis, using ImageJ (Rasband 1997-2018). 3.5 mm by 1 mm areas close to the absorption face, from the specimens' core, and close to the evaporation surface were reconstructed by stitching multiple SEM images acquired at 160x magnification. A median blur filtered was applied, and the consolidant distribution was highlighted through image segmentation, applying minimum thresholding.

Porosity and water absorption behavior

Total porosity and pore-size distribution were evaluated by mercury intrusion porosimetry on a 1 cm^3 volume of material. A sample representative of each different condition was investigated (after 120 days curing for the consolidated samples) using a MicroActive AutoPore V 9600.

The water absorption behavior by capillarity was investigated following a standard procedure (UNI-EN 2000) on 50 mm cubic specimens. At least three specimens were tested for each stone and curing condition. The effects of the treatment on the capillary water absorption were assessed using the Relative Capillary Index (IC_{rel}), calculated according to (Peruzzi, Poli, and Toniolo 2003).

3. RESULTS AND DISCUSSION

FTIR characterization of the consolidant under different RH curing regimes

All the characteristic peaks of TEOS are visible in the 4000-600 cm^{-1} spectral region at the initial stage of analysis of the fresh material (Figure 1 and Figure 2, red lines). In particular, the CH stretching modes of the alkoxy groups give sharp absorption bands at 2977, 2929, and 2893 cm^{-1} (Rubio, Rubio, and Oteo 1998). In the 1500-1200 cm^{-1} region, the peaks at 1485, 1444 and 1367 cm^{-1} correspond to the bending mode of $C\text{-}H_3$ and $C\text{-}H_2$ groups (Rubio, Rubio, and Oteo 1998; Tejedor-Tejedor, Paredes, and Anderson 1998), whereas the peak at 1393 cm^{-1} can be assigned to the symmetric $C\text{-}H_3$ bending (Tejedor-Tejedor, Paredes, and Anderson 1998). The most intense absorption peaks of liquid ethyl silicate are observable between 1170 and 800 cm^{-1}. In this region, the sharp peak at 1169 cm^{-1} is due to the CH_3 rocking mode, whereas the split absorption peak at 1105-1082 cm^{-1} is associated with the asymmetric C-O stretching mode (Wang et al. 2015). The very sharp peaks at 970 and 796 cm^{-1} are related to the C-H rocking mode and to the C-O stretching mode of the silica precursors, respectively (Innocenzi 2003; Wang et al. 2015).

The spectra collected at increasing curing times at 50% RH show the intermediate silanol formation and their final transition to Si-O-Si groups due to siloxane condensation (Figure 1). After the first step of curing (3 days), the initial reaction of ethyl silicate is highlighted by the depleted absorption peaks in the C-H stretching region due to hydrolysis, although no shifts are observed between 3000 and 2800 cm^{-1}. The same applies to the peaks in the 1500-1200 cm^{-1} region. The broad band centered at about 3360 cm^{-1} (O-H stretching) can be attributed to the formation of silanols. The main spectral differences at this stage are the change of the main split peak of the fresh ethyl silicate at 1105-1082 cm^{-1} into a single peak shifted towards lower wavenumbers (1058 cm^{-1}), being now associated with Si-O bonds (symmetric Si-O stretching). This can be linked to the progressive formation of siloxane groups resulting from the ongoing condensation reaction (Wang et al. 2015). The absorption peaks at 970 and 796 cm^{-1} are decreased in intensity and shifted towards lower wavenumbers (around 960 and 790 cm^{-1}, respectively) due to the formation of both silanol and siloxane species (Innocenzi 2003). The peak at 970 cm^{-1}, in particular, is also broadened compared to the fresh state and becomes asymmetric as silanes are hydrolyzed into silanols, as reported in the literature (Wang et al. 2015).

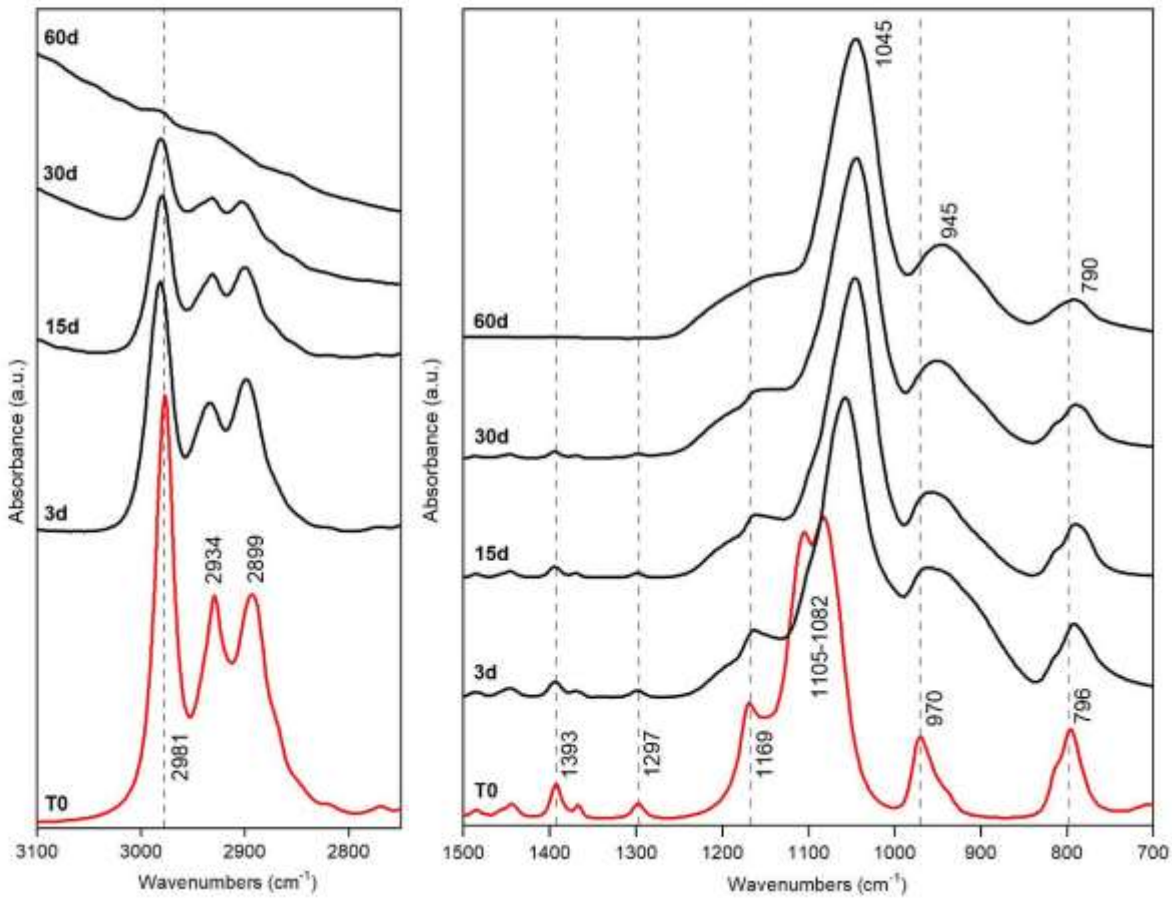

Figure 1 – FTIR spectra of ethyl silicate cured at 50% RH at increasing curing time (red line: pure ethyl silicate; black lines: ethyl silicate at 15-30-60 days of curing)

The progression of the hydrolysis and condensation reactions to form the silica gel after 15 and 30 days of curing is indicated by the additional decrease of all the absorption peaks attributed to the alkoxy groups. However, their residual presence, particularly between 3000 and 2800 cm^{-1}, suggests that the reaction is still not completed after 30 days of curing. The increasing presence of different hydroxyl species is also indicated by the broadening of the peak centered at 3365 cm^{-1} and by the formation of a peak at 1640 cm^{-1} due to the O-H bending mode of silanols. Silica gel formation resulting from the ongoing condensation is confirmed by the further shift of the main Si-O absorption peak to lower wavenumbers (1045 cm^{-1}), and of the peaks at 960 and 790 cm^{-1}.

The silica gel applied on microscopy glass slides completes most of the curing between 30 and 60 days. The C-H stretching absorption of ethyl silicate in the 2800-3000 cm^{-1} region is almost entirely reduced, and only two very low residual peaks around 2980 and 2930 cm^{-1} can still be observed, suggesting that most of the alkoxy groups have reacted. The C-H bending absorptions in the 1500-1200 cm^{-1} region are entirely consumed. The same applies to the C-H absorption of ethyl silicate at 1297 cm^{-1}. The peak at 1169 cm^{-1} detected in the fresh ethyl silicate is also progressively reduced to a shoulder. The further broadening of the 3365 cm^{-1} and the permanence of the O-H bending peak around 1640 cm^{-1} (data not shown) can be attributed to residual silanol groups or condensed water from the hydrolysis or condensation reaction (Wang et al. 2015).

A comparison of the 50% RH cured ethyl silicate and the 75% RH one after 15 days of curing shows significant differences in some of the spectral features (Figure 2). In the fingerprints region, the 75% RH cured shows a much more rapid depletion of the 1169 cm^{-1} peak related to the silica precursor, which is reduced to a shoulder centered around 1165 cm^{-1} (Si-O stretching absorption of the forming silica gel) (Barberena-Fernández, Carmona-Quiroga, and Blanco-Varela 2015). After the same curing time, this peak was still detected in the 50% RH cured ethyl silicate. The 796 cm^{-1} peak is decreased as well, and the hydroxyl species (either due to silanol formation and/or water condensation) are already formed at this stage of curing, as indicated by the broad peak centered at 1640 cm^{-1}. The C-H stretching absorption peaks in the 1500-1200 cm^{-1} region are less intense than the 50% cured. Overall, these changes suggest an increased polymerization rate due to the higher humidity condition (Barberena-Fernández, Carmona-Quiroga, and Blanco-Varela 2015). Nonetheless, a concurrent and more rapid consumption of the C-H vibrational modes cannot be clearly observed.

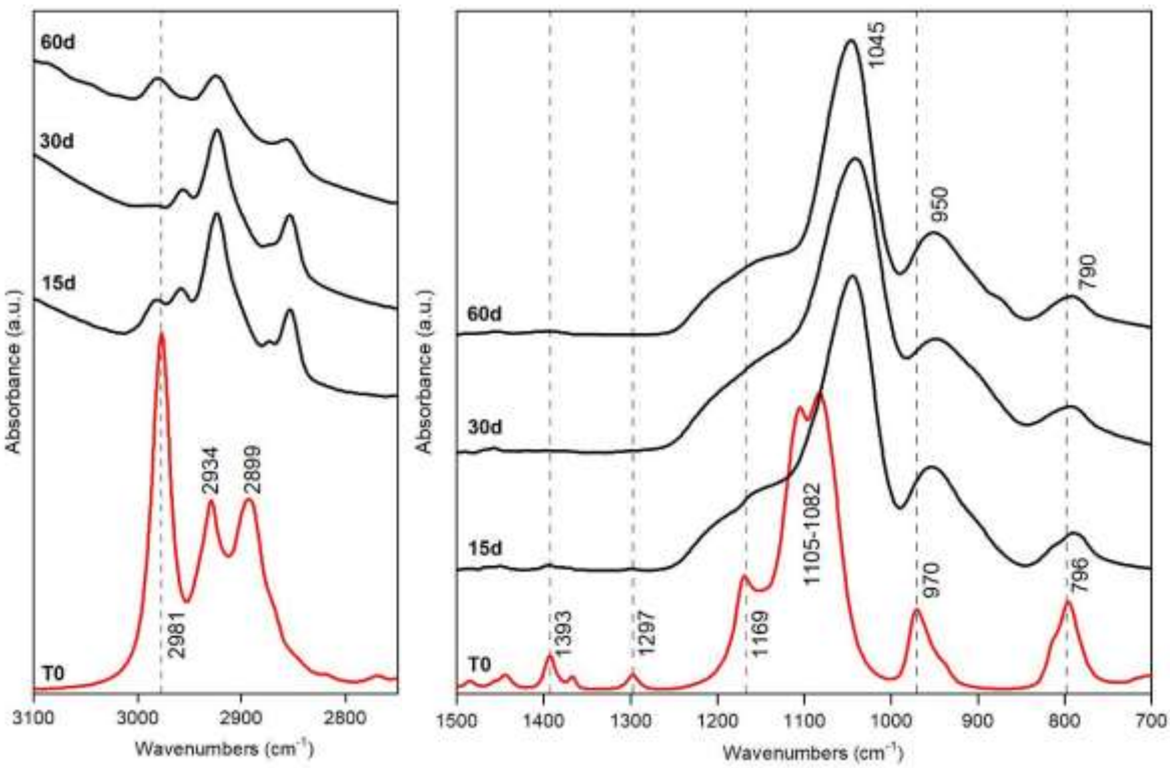

Figure 2 – FTIR spectra of ethyl silicate cured at 75% RH at increasing curing time (red line: pure ethyl silicate; black lines: ethyl silicate at 15-30-60 days of curing)

A similar trend is observed after 30 days of curing, with the same reduction of the shoulder at 1165 cm^{-1}, progression in the formation of hydroxyl groups, and permanence of the newly formed 2850 cm^{-1} peak. Unlike the 50% RH cured ethyl silicate, the absorption peaks related to C-H vibrational modes, particularly evident in the C-H stretching region, are still present after 60 days of curing in humid conditions and can be associated with the residual permanence of unreacted species. Such peaks are reduced but still detectable after prolonged curing (up to 6 months, data not shown).

Mechanical testing

3-point flexural-tensile test

The mechanical characterization results by flexural- tensile strength indicate that the selected curing regimes significantly affected the overall consolidation performance (Figure 3). The PS specimens consolidated and cured at 50% RH had greatly improved flexural-tensile strength after 28 days of curing (C50_28d in Figure 3, left), with an average 186% increase with respect to the reference untreated stone. An almost fivefold increase of the $E_{dynamic}$ was also detected. A prolonged curing time was beneficial to further promote the strength development, consistently with the FTIR results that showed ethyl silicate still reacting after 4-week curing. When curing time was extended to 120 days (C50_120d), the flexural-tensile strength reached a final average value of 5.5. MPa, corresponding to a strength increase of about 254%.

The humid curing condition (75%) generally decreased the strength development. A more limited flexural-tensile strength increase was observed at 28 days (C75_28d) in comparison with the specimens treated and cured at 50% RH. A similar trend was observed for extended curing times. After 120 days of curing (C75_120d), flexural-tensile strength continued to improve, but the ultimate strength development did not equal the one obtained at 50% RH curing (about 20% lower).

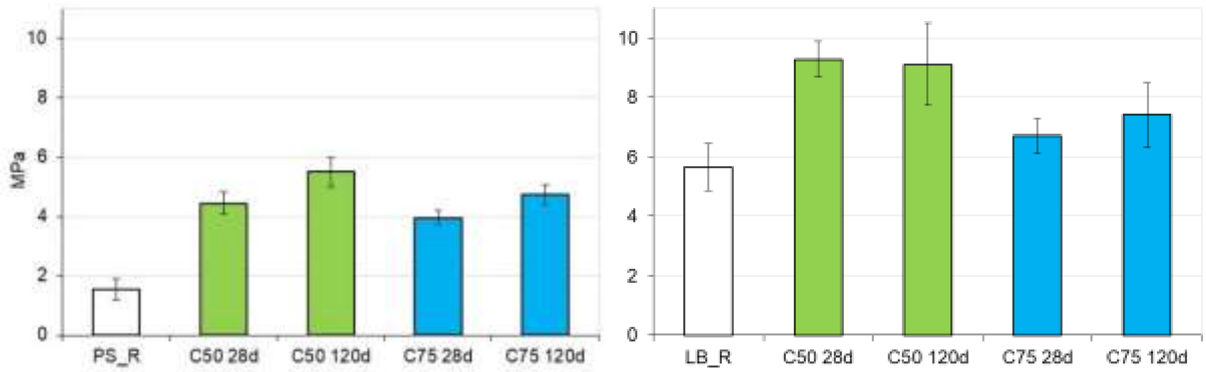

Figure 3 – Result of the flexural-tensile test (average values ± standard deviation, curing conditions and times area reported on the x-axis) of Prague (left) and Locharbriggs sandstone (right). Color codes: white, reference stone; green, after consolidation and curing at 50% RH (after 28 days and 120 days of curing); blue, after consolidation and curing at 75% RH (after 28 days and 120 days of curing).

The consolidation results of LB specimens were generally more limited than PS, consistent with the initial differences in the mechanical properties of the pristine substrates and the reduced consolidant uptake of LB. After 28 days curing at 50% RH (C50_28d in Figure 3, right), LB specimens displayed a 64% increase in flexural-tensile strength compared to the reference stone and an almost twofold increment of $E_{dynamic}$ (data not shown). Unlike PS, no further increase occurred when the curing time was extended to 120 days (C50_120d, t-test P value = 0.4).

Curing at 75% RH reduced the consolidation efficacy. The results after 28 days of curing (C75_28d) were only slightly higher than the unconsolidated stone (+18% increase). Similar to the 50% RH cured specimens, the strength development did not benefit from an extended curing time, as indicated by the values at 120 days (C75_120d), which showed no statistically significant difference compared to the 28-day one (t-test, P value = 0.06).

Drilling resistance measurements

Table 2 summarizes the DRMS results for each stone and treatment/curing condition. The average values elaborated from the DR curves in the 1-18 mm depth interval and after wear correction are reported in Figure 4.

As already indicated by the flexural-tensile strength results, PS experiences a more intense increase in the cohesion after treatment than LB when cured at 50% RH. The average DR of the consolidated stone is more than three times higher than the untreated reference substrate. Curing at higher humidity results in a more limited consolidation performance. The final DR increase in such a condition is limited to +82%.

Table 2 – Average DR results (standard deviation in brackets) and %DR increase after treatment

	Average DR (N)	%DR increase
PS reference	5.19 (±0.93)	-
PS 50% RH curing	18.01 (±2.49)	+247%
PS 75% RH curing	9.46 (±1.65)	+82%
LB reference	13.73 (±3.09)	-
LB 50% RH curing	22.58 (±7.36)	+64%
LB 75% RH curing	15.15 (±5.16)	+10%

As for PS, LB achieves the highest DR increase when cured at 50% RH, although the increase in mechanical cohesion is much more limited than PS under the same curing conditions. On average, LB showed a +64% increase after treatment and a higher data dispersion than PS. The latter can be attributed to the less homogeneous fabric of LB (i.e., mineralogy and presence of bedding layer) and lower porosity than PS, possibly resulting in a less uniform distribution of the consolidant within the pore structure.

According to the average DR results and the single specimens' values (Figure 4), the overall effect in terms of mechanical cohesion increase of LB at 75% RH is very limited.

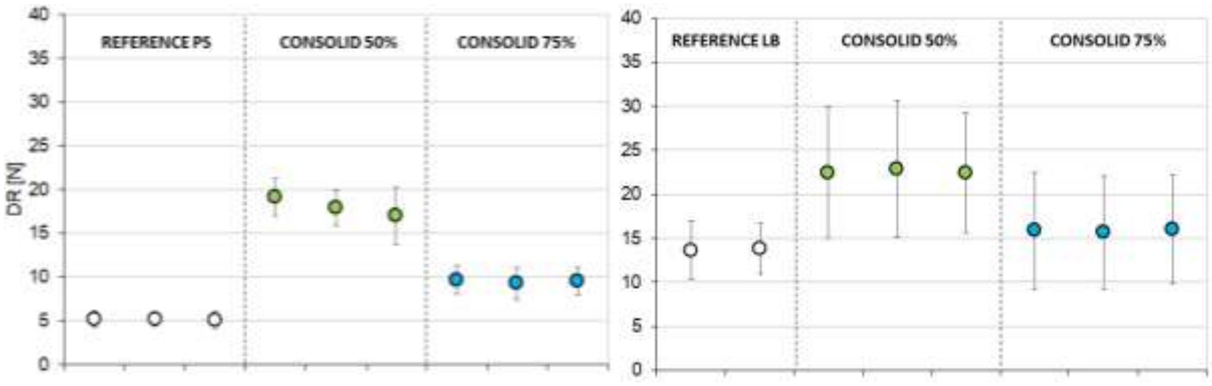

Figure 4 – average DR values (± standard deviation) of PS (left) and LB (right) before and after treatment and curing at 50% RH and 75% RH

Microstructural characterization

Scanning electron microscopy

Comparative SEM observations of thin sections of consolidated specimens were conducted at increasing magnification levels, targeting morphological differences in the silica gel, such as the extent of cracking, the gel-mineral interface features, and the overall distribution within the pore structure after the two curing conditions.

SEM images of PS cured at 50% RH confirm the full penetration of the consolidant within the stone specimen, as indicated by the presence of highly cracked silica gel unevenly distributed up to the evaporation surface. A slightly higher concentration is detected close to the imbibition and evaporation front compared to the bulk of the specimen (Figure 5, a-c). The newly formed xerogel partially fills the available porosity and follows the stone microstructural topography. At higher magnification levels, areas showing a good adhesion at the substrate/consolidant interface can be observed (Figure 6, left), as well as some limited bridging, although cracked in most cases.

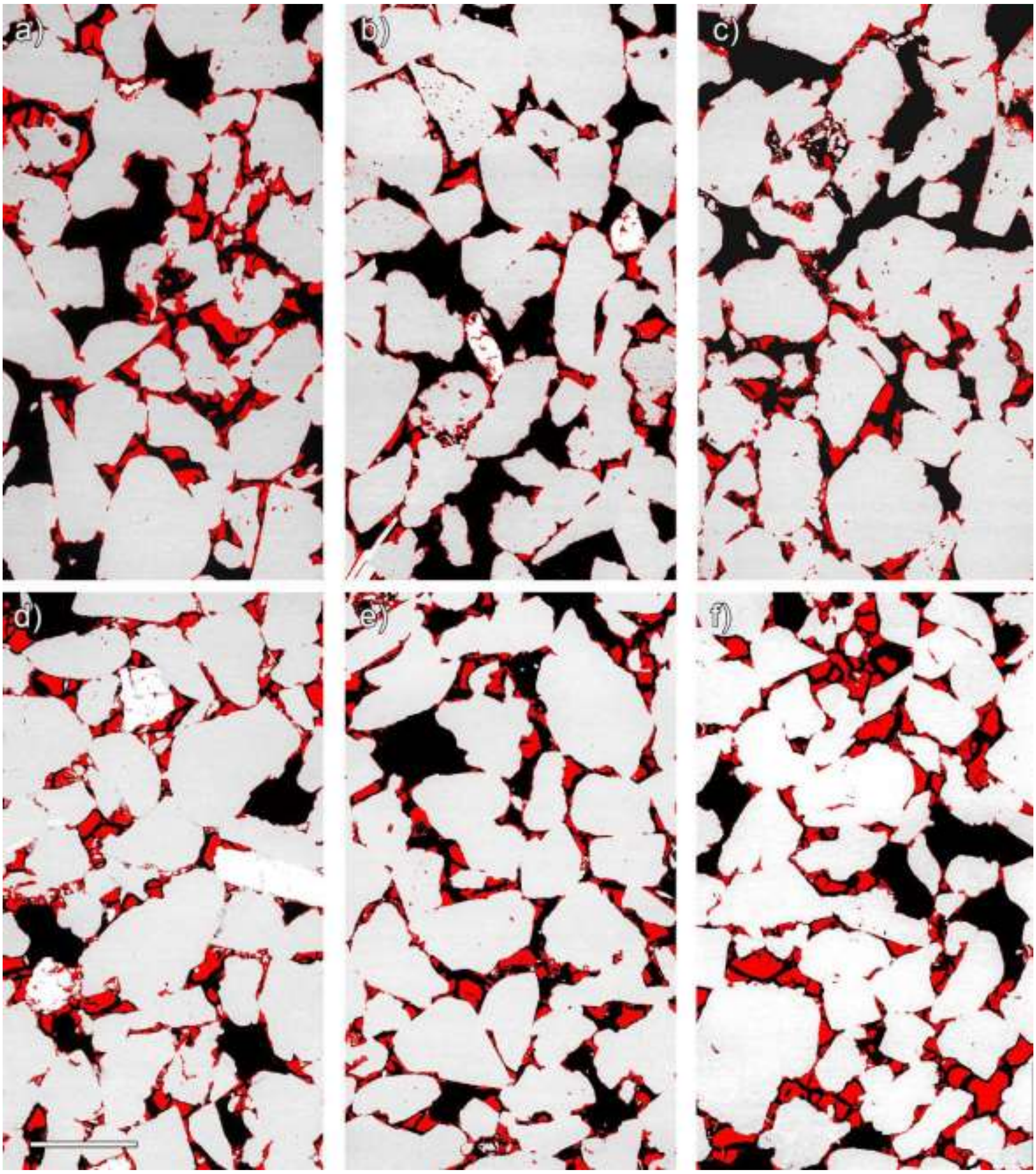

Figure 5 – SEM micrographs of consolidated PS thin section after 50% (a-c) and 75% (d-f) RH curing. Distribution of the consolidant (in red) close to the imbibition front (a, d), in the core of the specimen (b, e), and close to the evaporation surface (c, f). Scale bar = 300 µm

PS cured at 75% RH shows a higher amount of silica gel formed within the inter-particle spaces and more evenly distributed along the depth profile compared to 50% cured one (Figure 5, d-f). The gel clusters formed at 75% RH appear more rounded than the 50% RH counterpart, and the adhesion at the stone interface seems more limited (Figure 6, right). Moreover, the gel appears darker than the 50% one. Considering that all the acquisition parameters were kept constant, such a difference can be attributed to microstructural and/or compositional differences in the gel. These may include the permanence of unreacted organic groups from ethyl silicate, as suggested by the FTIR results.

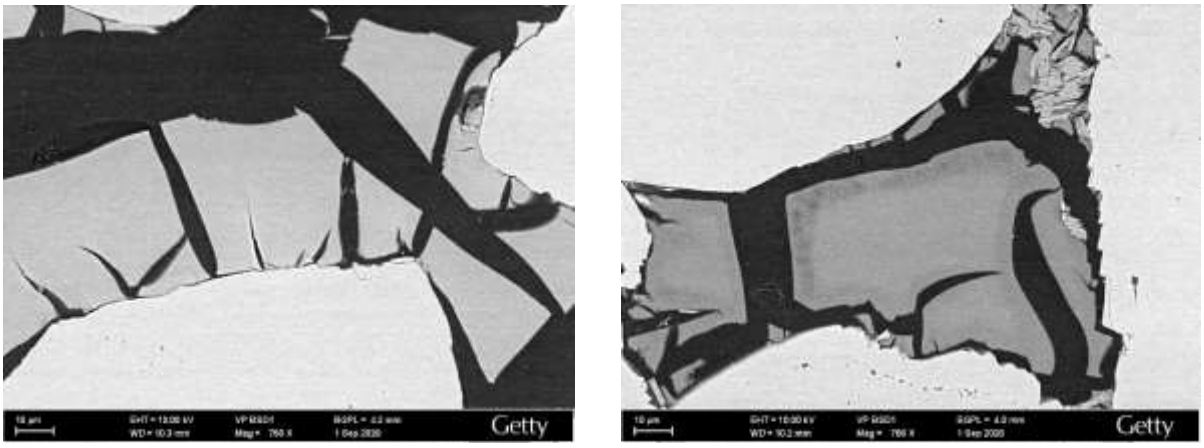

Figure 6 – SEM micrographs of consolidated PS thin sections: left) after 50% RH curing; right) after 75% RH curing (BSD images)

Overall, the amount of consolidant deposited in LB specimens and qualitatively detected by SEM is remarkably lower than PS. This is consistent with the different initial consolidant uptake of LB (half that of PS). SEM observations confirm the complete penetration of the consolidant throughout the entire depth profile. Under both curing conditions, LB showed a particularly uneven distribution of the consolidant. Higher concentrations are observed close to both the absorption and evaporation surface than the core. In the core area, the amount of gel deposited is particularly limited especially after 50% RH curing. A highly cracked gel is observed at 50% RH, with poor adherence to the substrate (Figure 7, left). In most cases, the presence of diffuse interstitial clay, visible as an irregular layer extensively covering the grains, prevents an effective bridging of the consolidant at the interface with the silica grains (Fig. 7, right). The gel follows the topography of the clay layers, particularly upon curing at high humidity conditions, and it is mostly detached from the substrate.

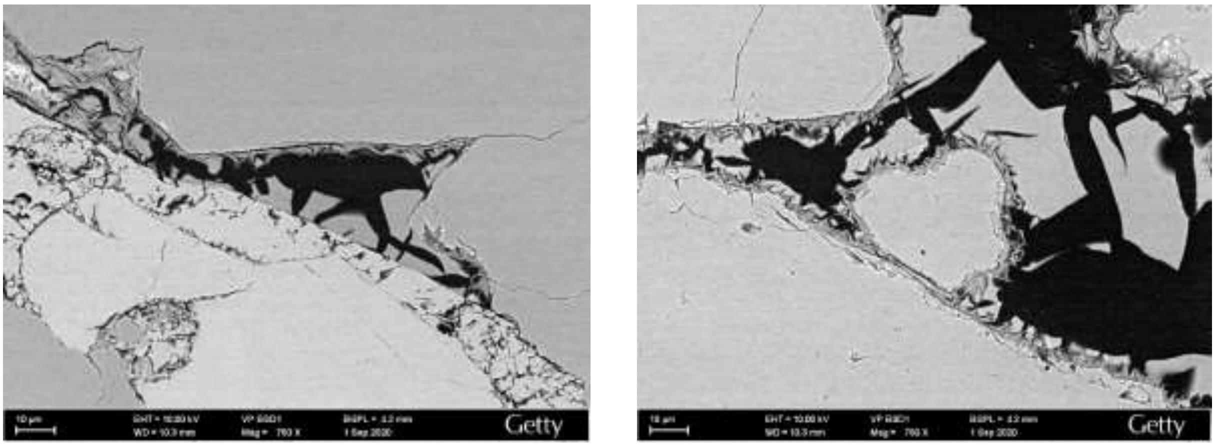

Figure 7 – SEM micrographs of consolidated LB thin section after 50% RH (left) and 75% RH curing (right) (BSD images)

Similar to observations for PS, curing at 75% RH promotes the formation of a darker gel than standard condition, characterized by larger clusters. Moreover, the amount of gel formed at high humidity and qualitatively assessed by SEM seems higher than the 50% RH.

Porosity and pore structure

MIP confirmed the microstructural changes induced by the xerogel formation and detected via SEM. Compared to the total porosity of the reference untreated substrates, LB undergoes a 12% and 19% reduction, and PS a 19% and 20% reduction, after treatment and curing at 50% RH and 75% RH, respectively. These results are consistent with the SEM observations, which highlighted a more intense inter-particle filling effect upon consolidation for PS and LB cured at high humidity.

The overall pore size distribution is altered as well (Figure 8). Due to the partial pore-filling and cracking of the silica gel after 50% RH curing, the original unimodal distribution of PS centered at 26 μm is split into two peaks. The main one is reduced but maintains the original distribution, while new slightly finer pores are created as indicated by the additional distribution peak around 11 μm. The ratio between the two new peaks is reversed after 75% RH curing. The initial distribution peak is further reduced and almost completely depleted, as most of the pores are shifted towards the finer diameters.

The LB trend is less clear than that for PS. The 50% RH curing seems to reduce the overall porosity without significant alteration of the pore size distribution, which shows an even narrower concentration of the pore around 14 μm. The high humidity curing causes changes that are more consistent with what is observed for PS. The distribution becomes bimodal, and the peak corresponding to the initial distribution is mostly depleted. In this case, most of the porosity is concentrated within a finer pore-size interval, around 6 μm.

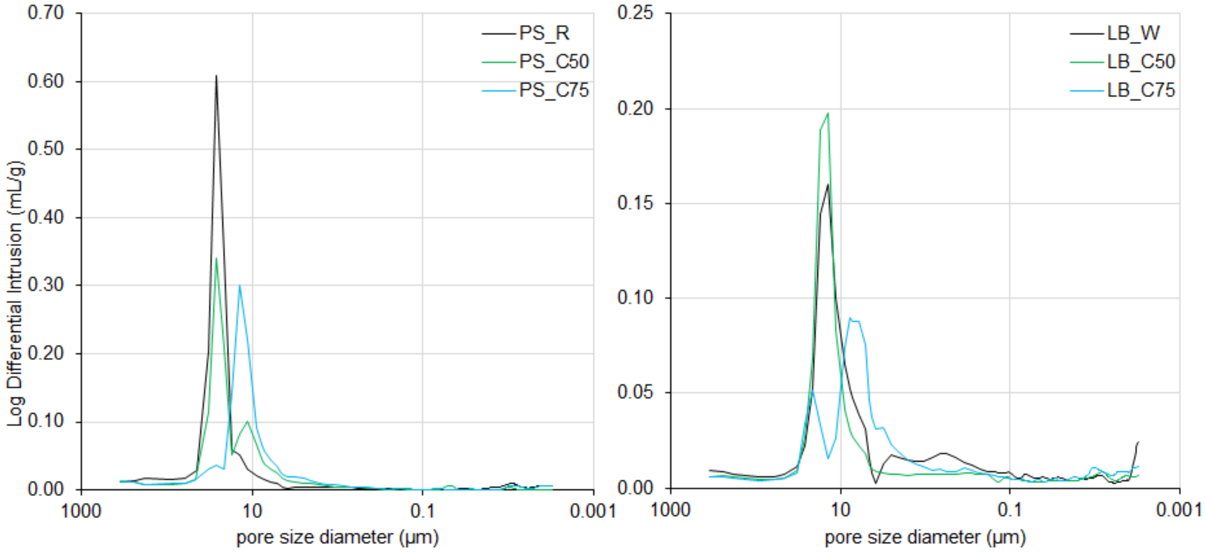

Figure 8 – pore size distribution of PS and LB specimens before (black lines) and after treatment and curing at 50% RH (green lines) and 75% RH (blue lines)

Water absorption behavior

As expected, due to partial filling of the pores by the xerogel, all curing conditions altered the capillary water absorption behavior up to different extents (Figure 9). After the treatment, the early stage absorption of both substrates – approximately within the first 20 minutes – is slowed down. The reduction under both curing conditions is particularly significant for PS, which was characterized by an extremely rapid early-stage absorption rate before treatment.

For LB, the most intense reduction of the initial absorption rate occurs after curing at high humidity, which can be linked to the consolidant accumulation at the treatment surface observed by SEM. In this case, the time required to reach an almost steady absorption is significantly delayed, and plateau conditions indicating the full saturation of the specimen at ambient pressure are obtained only after 3 hours of imbibition (steady conditions were achieved after 30 min of capillary absorption in the reference untreated stone).

The total amount of water absorbed by capillarity is decreased as well. The relative capillarity indexes show for both substrates an overall reduction of around 30% after curing at standard RH and 40% after high humidity curing (Figure 10).

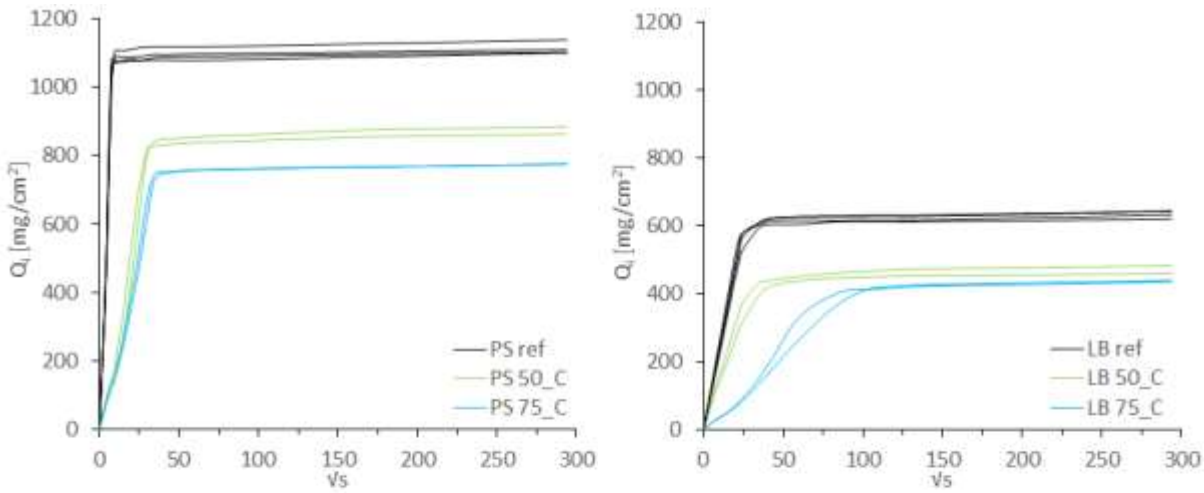

Figure 9 – Capillary water absorption curves of PS (left) and LB (right) reference specimens (black lines), and consolidated and cured at 50% RH (green lines) and 75% RH (blue lines)

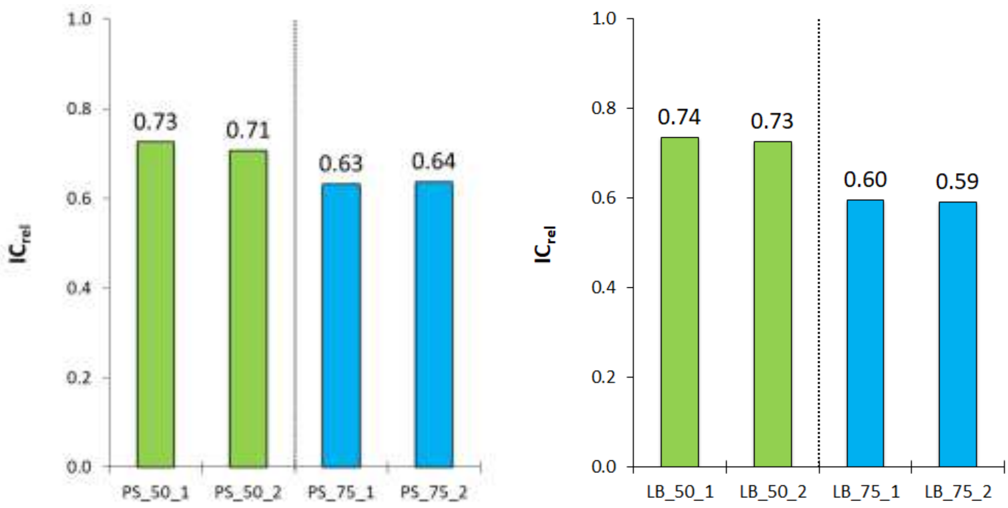

Figure 10 – Relative capillary indexes of PS and LB specimens calculated before/after consolidation. Color codes: green bars: 50% cured specimens; blue lines: 75% cured specimens

4. CONCLUSIONS

The overall effect of curing regimes at different RH (50% and 75%) on the consolidation efficacy of a commercial ethyl silicate was studied on two sandstones, targeting microstructural and mechanical variations. The main chemical changes following the evolution of the xerogel under the two curing conditions were also monitored on the consolidant applied to microscopy glass slides.

The RH conditions during curing significantly affected the performance of ethyl silicate in both substrates, and the multi-analytical characterization approach provided a comprehensive overview of the treatment results, combining lab-based and portable methodologies to assess the change in the mechanical properties.

The results showed that the selected ethyl silicate effectively improves the mechanical strength of both substrates at the reference curing condition, with respect to the flexural-tensile resistance and cohesion assessed by drilling resistance measurements. The strength increase was much more limited when curing was conducted at RH higher than the reference one, despite the higher reactivity of the consolidant in the former condition. The reduced consolidation efficacy was particularly relevant for Locharbriggs sandstone.

The microstructural characterization of Locharbriggs also indicated a poor bonding of the silica gel, and the role of the clay minerals requires further investigation. The silica-gel formation within the pore network of both stones reduced the total porosity and altered the overall pore size distribution, and the formation of finer pores was observed after curing at high humidity. In such a condition, a significant alteration of the capillary water absorption behaviour was also observed, in particular for the early-stage absorption rate of Locharbriggs, with possible implications on the long-term performances of the treated substrates.

Future research directions include the investigation of the microstructural features of the xerogel formed at different curing conditions, the effect of the RH regime on the reaction rate of the consolidant deposited within the stone pore structure, and the impact of different treatment conditions (e.g., dilution, application methodology) on the consolidation mechanism.

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Bridging the gap between science and practice. Communicating research information

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SUMMARY: Scientific production in stone consolidation and stone conservation in general is overwhelming, but there is a persistent feeling that it is too specific, complex or distant from reality to arouse the interest of professionals who work directly on conservation problems. This feeling is translated as a gap between science and practice, possibly an exaggeration, but which is not beneficial for stimulating inter-collaboration and achieving better conservation interventions.

The authors consider that more than blaming any part of the equation, it is necessary to assume that scientists and researchers need to do more and communicate better to reach the interests and concerns of professionals. We also assume that not all papers, theses or research reports need to have direct, immediate, and unequivocally applicability, under the accepted concept that basic science and base-line research will sooner or later have positive impacts on practice. However, knowing this fact, we also sustain that worse than the absence of direct applicability, is the inclusion in scientific papers of alleged solutions but with insufficient justification and validation of data.

Based on experience, we will try to identify some common trends found in scientific papers about alleged "practical applicability" of the reported results, and point out some basic "rules" for the concerned researchers to use to increment their contribution for the solution of practical problems.

KEY-WORDS: stone consolidation; communication in science; practical problems

1. INTRODUCTION

Scientific research on cultural heritage topics is carried out worldwide in hundreds of research centres. Publications on stone conservation were scarce before the 1970s, but today they are abundant, diverse, and possibly excessively dispersed and diluted in the vast domain of scientific journals.

Despite this abundance of scientific information, there is a feeling among professionals in the practice of stone conservation, especially conservator-restorers, that research and scientific information are developed in an area that is difficult to access and often presenting unclear proposals, and of questionable applicability for the solution of real conservation problems. These differences in the perception of the contexts and objectives of the respective domains create a discrepancy between science providers and possible recipients, which is felt as an existing gap between science and practice. Despite the strong benefit that professionals in stone conservation are taking from the multiple scientific fields, this gap is felt.

The lack of mutual engagement is perceived in the small number of practitioners who generally participate in scientific meetings on stone conservation matters. Multiple reasons can be pointed out to justify this situation, for example the low expectation that improvements relevant to the practical world will be presented is certainly one of them. Yet, scientific research produces new materials and products, proposes new methods as well as the improvement of old ones, offers new diagnostic and control tools, and proposes new interpretation models and new documentation methods.

The problem is not new, and reasons have been put forward to explain and resolve it. In writing the Torun guidelines (see (Doehne and Price 2010), page 68) for organizing stone conservation conferences, the committee members emphasise the need for better event planning and stricter selection processes. These concerns were extended and detailed by those authors (Doehne and Price 2010) who stressed that quality should prevail over the ever increasing quantity. They feel that a lack of focus of the research themes is a real risk, since "…*there is still a danger that research can become so theoretical that it loses sight of its main purpose*", while stating that "*There is no point in doing research unless the outcome can be applied in practice. This does not mean that there is no place for long-term, strategic research, but that any worthwhile research must ultimately contribute to the care and conservation of the heritage*."

The emergence of low quality publications is and will continue to be a common occurrence, and the quick and simple screening processes used by many "well evaluated" journals indicate that even the so emphatically recommended peer-review process may no longer be a secure quality assurance. On the other hand, it is important to recognise that science is being produced by researchers with multiple backgrounds and multiple personal and institutional motivations, and it is not simple to identify what is *"worthwhile research"* which is demanded for its goal that it "…*must ultimately contribute to the care and conservation of the heritage*".

The current situation shows that putting all the emphasis on research quality alone has not solved the communication problem between science and practice and has not helped professionals to get the most out of the high quality research being done. It is probably time to change course and, instead of focusing on quality alone, redirect the focus to the way science is communicated vis-à-vis stone conservation professionals, its end users and key players. This implies changing paradigms from "communicating what" to "communicating how".

A basic and fundamental concept of this new paradigm is to keep in mind that not all research projects or scientific publications, in cultural heritage in general or in stone conservation issues in particular, necessarily need to convey or provide an immediate solution for a real problem or to have a clear practical impact. Therefore, users should not obsessively seek solutions in all scientific articles or reports, and scientists should not be tempted to present explicitly or implicitly any suggestions for practical application with insufficient data validation and lack of practical demonstration.

In this article, the authors consider that better communication between science and practice is needed and sustain that scientists should and could do it more profitably. A necessary step is to clarify the roles and explain each other's purposes when communication is attempted.

2. WHO IS DOING WHAT? WHAT IS THE CONTEXT AND PURPOSE?

Understanding the role that each one has, the adequate consideration of the work context, and a clear definition of objectives are the steps to be followed.

Roles, contexts and objectives can be combined and vary over wide limits, and each combination will have its own perspectives and responsibilities in terms of communicating the scientific result. A few examples can be:

i. A scientist working under a research grant from a scientific organisation,
ii. A student preparing a MSc or a PhD thesis,
iii. A scientist working for a museum, an archaeological site, or any public authority,
iv. A researcher working for a products developer and provider,
v. A conservation scientist working as consultant or as work supervisor.

All of them may be dealing with relevant cultural heritage topics, working with heritage materials or objects and sooner or later, all their efforts and achievements can result in significant benefits to conservation practice. However, not everyone necessarily needs to conclude their paper or report with a solution or recommendation for direct and immediate practical application.

A study on the influence of different minerals in the curing process of a consolidant, the monitoring of the degradation of a product under UV radiation, the evaluation of the applicability of a new measuring instrument, are examples of concrete and well-defined subjects and generally their authors are not tempted to conclude with any practical solutions or recommendations. As these are well-defined contexts and objectives, scientific results will be received by interested users, who will eventually mediate them for any possible practical use.

In stone conservation, especially when dealing with consolidation issues, a great deal of ambiguity is often present in the published literature. A research model that uses some types of stones and some consolidation products, tested with a few characterisation methods, is representative of the work program used in many published articles. There is nothing wrong with this model, except when extrapolations to the real world are advanced or concrete practical recommendations are made based on insufficient evidence of the predictable implications they may involve.

2.1 The academic context

Most of the produced literature in stone conservation comes from the academic world and is found in journals and conference proceedings. The preparation of theses and work on projects with institutional funding are typical research environments in the academic world. This research community has enormous potential and it is beneficial for the practice of conservation that it continues to have cultural heritage as a relevant research domain. The main paradigm of this research environment is the production of new knowledge, which must be accompanied by an absolute freedom to choose the research topics. Under this understanding, it makes no sense to blame publications issued from such a community for insufficient practical focus or lack of clear indications to solve conservation problems. These publications should be evaluated by their peers for their scientific content, and direct applicability should not be taken as an evaluation criterion, unless the authors explicitly mention it as one of their research targets.

As a corollary to this understanding, researchers working under this paradigm would be expected to refrain from jumping to practical guidelines or recommendations when unsufficient evidence of practical validation is included in their research results. Of course, they should not be discouraged from embracing more practice-oriented themes but doing so they will enter a new group of science providers with specific needs and therefore certain obligations will have to be assumed.

2.2 The pre-practice context

Many scientific publications can be considered as produced under a pre-practice paradigm. They use heritage items or materials, address one or more practical problems, and make considerations potentially usable in conservation practice. What makes these studies specific is the authors' willingness, explicitly or implicitly assumed, to contribute directly to the practice of conservation and to have their results adopted by conservation professionals, especially conservation scientists and conservator-restorers.

When assuming a closer proximity to and aiming at having a more immediate impact on conservation practice, these researchers must simultaneously assume that the information they are producing will be absorbed and processed by professionals with limited research resources and under strict time constraints. The use of accessible language in their scientific analyses and the construction of syntheses from them are highly propitious elements for success.

While the previous cluster has no obligations other than producing good quality science, researchers who assume pre-practice-oriented objectives acquire some more specific obligations. The target problems must be properly presented and characterised and the surrounding context necessary to understand and interpret the research results must be properly described. Authors should always keep in mind that the end users of their research will certainly have to adapt the conclusions to situations that differ to a greater or lesser degree from those that were the subject of the study. As stated elsewhere "*The information will no doubt be of value to those who are concerned with the care of that particular monument, but it is of questionable relevance to a wider audience unless the properties of the stone can be linked to its performance*." (Doehne and Price 2010).

Communications with the greatest chance of success are those that offer indications of how to consider any variations in the intensity of the problem that has been studied and any small or large differences in the properties of the materials. As well as those that offer better insights on how to master a conservation procedure, to adapt a test tool to field situations, or to decrease or increase a given conservation action.

Many studies in this category could be called "validation studies" (see another article in this symposium, (Delgado Rodrigues 2021)), which is possibly the cluster with the most useful source of information for stone conservation professionals. Communications of this type with validations of any kind as an objective must clearly describe which items of validation are under scrutiny and which are the validity limits of the main conclusions reached. A validation made with a limestone of 10% porosity cannot be extrapolated uncritically to a similar lithotype with 30% porosity. The results obtained in non-deteriorated, regular-shaped samples cannot be transposed to severely deteriorated stone surfaces without proper validated assumptions.

Authors should be aware that professionals have significant time constraints and generally lack the resources to spend long periods of time researching literature and interpreting excessively complex descriptions. Therefore, to better reach target users, publications should be written clearly and provide clues to allow readers to grasp more quickly the conclusions presented there. For example, instead of simply using limestone as a keyword, give an indication of porosity (low, medium, high porosity); instead of simply indicating consolidation, specify whether it was done on quarry samples, deteriorated samples, on-site tests; for a stone cleaning study, provide keywords about the method, samples, dirt, assessment tools, etc.

While publications of this type are not expected to provide direct solutions to complex conservation problems, they may be relevant in finding clues to a particular detail of the problem, to clarify a treatment protocol, to help interpret an unexpected aspect of actual conservation action, etc. When these potential objectives are considered in the layout of the publication, everything is closer to having more significant impacts.

It is not uncommon to find publications on stone consolidation following the format usually accepted for a selection procedure, using some types of stones, certain consolidants, and several tests to evaluate the effectiveness, harmfulness, and durability of the treatments. They often conclude by saying which product is the best, or just indicating that one is better in some ways while the other is better in others.

Publications of this type introduce more confusion than benefits in the practice of stone conservation. They are prepared in academic contexts, using a methodology more typical of the pre-practice context and the results tend to be weak in both. They do not reproduce well any concrete conservation problem, which implies that their conclusions are not directly applicable to any real situation. When no indication is given on how to transpose the results into the real world (the most common situation), then no obvious benefit is easily derived from them.

An appropriate selection of a conservation treatment will necessarily begin by characterising and explaining the concrete conservation problem and moving bottom-up to find the appropriate combination of a product and a treatment protocol. By adopting a bottom-down perspective, assuming that it is possible to select an "appropriate" treatment regardless of the target's concrete situation, this is equivalent to shooting in the dark with very little chance of success.

Obviously, crossing borders from the academic to the pre-practice context is admissible and even desirable, but it is highly recommended that the authors take into account the characteristics of each context and define their research plan fully aware of what the scientific and professional fields expect from them.

At the end of the day, all information with direct or indirect connection to stone conservation may eventually have impact on the conservation practice, but along the way may have to be taken before the relevant actors incorporate it into their toolkit. As wisely said by Giorgio Torraca some 40 years ago "*…scientific concepts and modern materials have obviously influenced modern conservation practice, but only insofar as they have been absorbed, more or less correctly, by the conservators who tried to adapt them to their needs*" (Torraca 1982).

2.3 The innovation and development contexts

The activity of innovation in materials, instruments and methods is not overwhelming, but it constitutes an important source of information in conservation science. In general, the authors are concerned that the result should be quickly incorporated into the research and professional areas, but a too fast move may result in skipping some essential intermediate steps.

The authors of such publications should keep in mind that their findings need appropriate validation by peers and, therefore, should avoid emphasising definitive conclusions about their end use and guarantee of results. For example, developers of a new consolidation product should indicate all possible details about its composition, chemical and physical properties and potential generic uses, but should refrain from recommending it as a solution for any specific situation or problem.

The introduction of new products in the conservation market is highly valued, but communicating information about a new product must be different from advertising it. What you expect to find in publications of this type are correct explanations of its conservation action, a description of the working principle, and indications of any preliminary results carried out under controlled conditions that help to inform what the product is and what is its purpose.

The fair play of all actors is necessary to raise standards of conservation and to avoid old established impressions that "*It is not infrequent to see research, development, production, and (positive) evaluation of the result carried out by the same person*" (Torraca 1982).

2.4 The professional's context

Publications on concrete problems and respective solutions coming directly from professionals are found in monographic documents and more rarely as case studies. Such documents have a low rating in terms of scientific impact and tend to be considered low quality information sources. In some favourable situations, the collaboration of professionals and scientists is possible, which can lead to a broader discussion of problems and the developing of conservation solutions.

Except in very specific and relatively rare situations, the resolution of concrete problems does not have the possibility of resorting to a specific research project to support it. Therefore, professionals must use the existing knowledge available in the published literature to obtain the scientific support necessary to solve their problems.

Consequently, the production of new knowledge is not a primary objective, which is why publications produced in contexts of this type are often underestimated. Instead, they are one of the best and irreplaceable resources to help build “experience”, an invaluable tool for anyone working with real conservation problems.

Publications on case studies are often misinterpreted in terms of their real importance and impact. Certainly, not all case studies contain high quality information, and it would be highly desirable for higher quality standards to be used in such publications. Purely descriptive texts may be of little interest, while clear and sustained discussions about the options taken and the methods used can be worth reading.

Again, the question is not "what" is communicated, but "how" it is communicated. A useful case study is not only listing problems, materials and methods used, but also discussing how the understanding of problems was achieved, what conservation options were under discussion, what information was relevant to decision-making, which were the site restrictions identified and how they were overcome, how social and legal variables were taken into account, etc.

3. WHAT MAY PRACTITIONERS EXPECT FROM A PROBLEM-ORIENTED RESEARCH TOPIC?

When deciding to write this text, the authors considered that there is a general perception that collaboration between scientists and professionals is scarce and that communication of information needs to be greatly improved. Inter-professional collaboration cannot be promoted by decree and it is unreasonable to expect that substantial improvements can be achieved in this area. The two work contexts with their respective resources and time constraints are so different that full collaboration is likely to continue to be limited to a small number of fortunate cases.

Research contexts and paradigms are largely driven by funding resources and, therefore, motivation and outcome are not expected to change the real situation between the academic and professional fields. What would be desirable is that researchers have a clear awareness of the distance or proximity they are from the practical world and define the objectives of the research in terms of this distance. Every researcher can provide insightful information, but only insofar as they do not intend to play the role of an actor they are not prepared to take on.

Researchers working in a “pre-practice” context, as defined above, have special responsibilities when they assume that they are working to validate previously established conclusions, to help clarify promising processes, or to translate theoretical knowledge into operational actions.

The information in this context is the main source of knowledge for professionals and it is worth exemplifying what are some of the common expectations that professionals place in their search in the scientific literature. Underlying these expectations are some common questions: how do these results help explain my own problem? How can I extrapolate these conclusions to solve the situation at hand?

The practitioner is working with a narrow and concrete domain, a specific stone, in a specific situation and affected by a number of problems and will seek information to solve them. On the contrary, researchers tend to favour wider scope themes to reach broader audiences. At least those who wish to follow practice-oriented research are expected to provide clues for professionals to adapt the broad scope of the research to their current narrow-scope conservation problem.

These clues should give clear indications of the type of materials to which the conclusions can be applied. This needs to include the target petrographic group, but also some relevant properties that can influence the results, for example, porosity, presence of clay minerals, etc. If information on performance indicators is discussed, precise indications of how to achieve them should be given for cases where the practitioner is dealing with a different stone or with a different porosity. And above all, it must be clear that the results obtained in the laboratory with “perfect” samples and under controlled working conditions are not directly transposable to conditions onsite where nothing is “perfect” and where few things are fully controllable. In short, a practice-oriented research study that aims to be of direct use by professionals, even when it deals with seemingly concrete research topics, must include clear indications on how its results can be transposed and adapted to solve the problems addressed in the study.

4. CONCLUSIONS

Progress in the practice of conservation has largely benefited from research carried out in academic contexts and in research projects of the most diverse types, depth, and objectives. However, a certain mismatch between the scientific and practical fields has always been felt, a situation that the authors attribute to a gap in the communication that they feel exists between the two domains.

It seems clear that the main reason must be attributed to us, researchers, for our unclear understanding of what professionals expect from us. Freedom of research is a blessing to the scientific world, but it can become a nightmare for professionals who try to move within this “wild” world of scientific information. Focused research topics are necessary for professionals, whether they are the exclusive target or when integrated into broader projects.

There are no magical solutions to this continuing deficit, but it is our belief that the communication of scientific information can be significantly improved, and this could help to bridge the gap with relevant benefits for professionals.

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Nanomaterials against stonework deterioration: where are we now?

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SUMMARY: Deterioration of stone materials in artworks represents a crucial problem in the field of Cultural Heritage preservation and/or restoration. Typical degradation phenomena are associated to environmental factors and air pollution, quite often unavoidable. Together with these issues, biodeterioration causes long term damage and irreversible alteration of the substrate. In order to limit such processes without altering the aesthetic and historical values of the artwork, cleaning procedures and consolidating treatments are generally applied to recover the degraded materials as well as decreasing the deterioration rate. In this regard, nanomaterials and nanostructures provide valid tools to support the historical monument preservation. In this contribution, an overview on the state-of-the-art nanomaterials employed in the preservation of historical stone monuments and on hybrid strategies investigated in our research group are provided.

KEY-WORDS: nanostructures, (bio)deterioration, antimicrobial, ZnO

1. INTRODUCTION

Typical degradation phenomena of stone artworks (e.g., sanding, black crust formation, soluble salts crystallization, etc.) are associated to environmental factors and air pollution. Additionally, the colonization of different living organisms on stone substrate gives rise to their biodeterioration, a complex process resulting in a change of appearance and durability of the material. Bacteria, algae and fungi are responsible for the formation of a biofilm on the substrate which interacts with the stone, causing long term damage and irreversible alteration of the substrate. In general, the climatic factor and atmospheric pollution can make the artwork decay process faster. In fact, they are irremediably exposed to rain, light, physical erosion, humidity and temperature changes. Anthropic activities increase the concentrations of SO_2, NO_x, and VOCs (volatile organic compounds) species in the atmosphere that eventually lead to the corrosion of artistic substrates, contributing to the degradation of works of art (Dei and Giorgi 2013).
For these reasons, it is crucial to find options and methods to limit (bio)deterioration processes, without altering the aesthetic and historical values of the artworks. According to the nature of monument materials, cleaning procedures and consolidating treatments are generally studied and applied to recover the degraded materials as well as decreasing the deterioration rate. Starting from the second half of the 20th century, synthetic polymers, such as acrylic resins (e.g. Paraloid B72), vinyl, silicone, and epoxy resins (e.g. EP2101) have been enthusiastically used for the consolidation and protection of stone and wall paintings, mainly because they were thought to be highly resistant to aging and easily removable. Unfortunately, synthetic polymers undergo degradation, resulting in the significant alteration of their visual aspect (mainly yellowing) and the strong alteration of physicochemical properties of the original substrates, such as porosity, water capillarity, water vapor permeability, and surface wettability (Piero Baglioni et al. 2013). In particular, the organic polymers should be selected according to the artwork materials. Other approaches based on alkoxysilanes (silicone resin material, e.g. tetraethyl orthosilicate-TEOS) are effectively useful for the protection of sandstone and granite. However, they presented many disadvantages when applied for the protection of carbonate-based artifacts, because they cannot effectively prevent the cracking and deterioration of carbonate stone (Xu, Zeng, and Li 2019). More specifically, the absence of free -OH groups in carbonate minerals, which could act as anchor sites for

silanols, is commonly referred as an important reason for the failure of TEOS-based consolidants (Sena da Fonseca et al. 2019).
Hence, it is clear that a continuous cutting edge investigation about Cultural Heritage protection and the development of innovative materials are necessary. In this sense, material science plays a key role. Nanoscience and nanotechnology, especially colloid science, may address a significant number of issues in the field of Cultural Heritage, in particular for the conservation and (bio)deterioration of artworks (Figure 1). Without doubts, the manufact conservation requires a multidisciplinary approach which combines material science, microbiology and environmental science, along with many other scientific disciplines. Specifically, the nature of both the artifact materials and the consolidant materials must be clearly established, as well as their interactions and the consequent properties. In such direction, this work aims to present a brief overview of the innovative nanomaterials employed in the preservation of historical stone monuments. The studies, the specific features and the applications of some nanostructures are discussed in this work, with a view of the future challenges and the development requests.

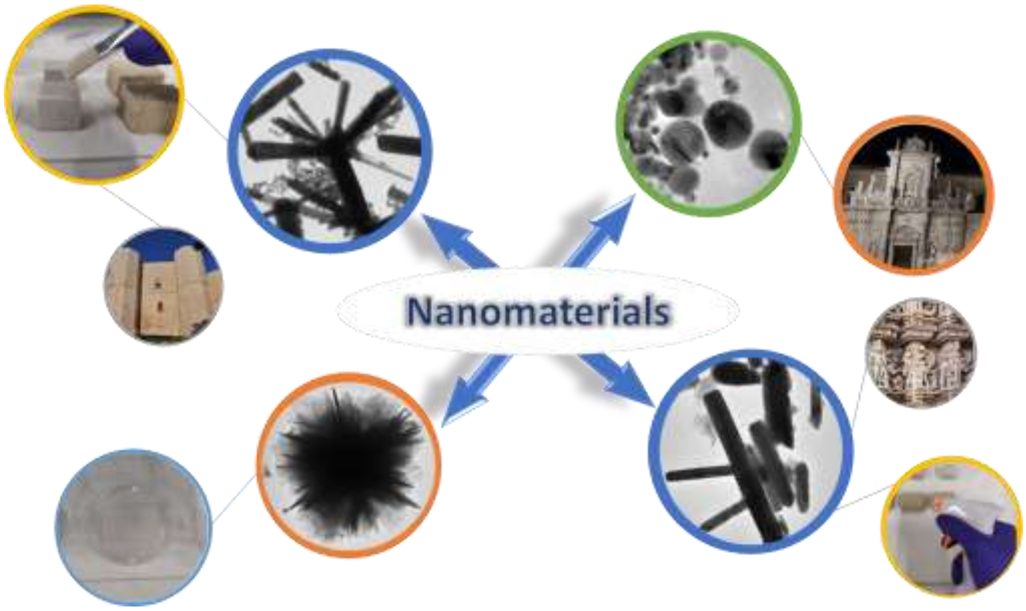

Figure 1: Nanostructures for coating preparation, which are useful to fight (bio)deterioration of stone artifacts.

2. NANOMATERIALS IN CULTURAL HERITAGE APPLICATIONS

Since '80s, Nanoscience has revolutionized a wide range of scientific fields, including the Cultural Heritage. (Piero Baglioni, Chelazzi, and Giorgi 2015). In particular, the nanometric size is helpful to facilitate the penetration through porous matrices, ensuring the unique NP task also in the manufact bulk. As a consequence of this, nanostructures induce an improvement of some material features which are essential for Cultural Heritage. Tab. 1 reports some practical examples of nanostructures studied for these applications. The following sections expound some details of the papers cited in the table, with particular focus on the alkaline earth metal hydroxide NPs and the metal (oxide) NPs.

Table 1. Examples of nanomaterials developed and applied to Cultural Heritage. The products marked with * are commercially available.

Material	Main features	Physical form	References
MgONPs	Antibacterial activity	Powder	(Castillo et al. 2019)
$Ca(OH)_2$NPs *Nanorestore®, CaLoSiL®	Consolidation and conservation	Powder	(Rodriguez-Navarro and Ruiz-Agudo 2018)
$Ba(OH)_2$NPs	Consolidation	Powder	(Giorgi et al. 2010)
$CaCO_3$NPs	Deacidification	Powder	(Bicchieri et al. 2017; Burgos-Cara et al. 2019)
AuNPs	Cleaning	Solution	(Gherardi et al. 2019)
SiO_2NPs	Superhydrophobic/oleophobic, and water repellence	Gel solution	(Mosquera, Carrascosa, and Badreldin 2018; Chatzigrigoriou, Manoudis, and Karapanagiotis 2013; Ntelia and Karapanagiotis 2020)
TiO_2NPs	Protection, antifungal activity	Solution	(Shu et al. 2020; De Filpo et al. 2013; Abbate and D'Orazio 2017; Gherardi et al. 2016)
AgNPs	Antimicrobial activity	Dispersion	(Carrillo-Gónzalez et al. 2016; Becerra et al. 2018)
ZnONPs	Antimicrobial activity	Solution	(Ditaranto et al. 2015)
CuNPs	Antimicrobial activity	Solution	(van der Werf et al. 2015)
Graphene oxide and carbon nanotubes	Nano-reinforcement	Powder	(Dimou et al. 2020)
Hydroxyapatite NPs	Restoration	Powder	(Mahmoud 2019)
Halloysite Nanotubes	Reinforcing agent	Powder	(Cavallaro, Milioto, and Lazzara 2020)
$Ca(OH)_2$/ Graphene Q Dots	Wall painting preservation	Powder	(Zhu et al. 2018)
$CaZn_2(OH)_6$	Consolidation and antimicrobial	Powder	(De la Rosa-García et al. 2018; Soria-Castro et al. 2019)
$Ca(OH)_2$/ZnO	Consolidation/Treatment kinetics	Powder	(Becerra et al. 2019)

Alkaline earth metal hydroxide and oxide NPs

The use of alkaline earth metal hydroxide NPs is extremely effective in the field of wall paintings and carbonate stones conservation. Indeed, $Ca(OH)_2$ turns into $CaCO_3$ upon carbonation, providing a crystalline network that is cohesive with the carbonate substrate, and mechanically reinforces the degraded surface (P. Baglioni and Giorgi 2013). In addition to that, calcium and magnesium hydroxides have proven to be excellent compounds for the deacidification of cellulosic works of art (Piero Baglioni et al. 2013). At the end of the '90s, Prof. Baglioni and researchers at CSGI (Center for Colloid and Surface Science) at the University of Florence, originally developed the first formulation based on calcium hydroxide nanoparticles in isopropanol (Ambrosi et al. 2001), which has been further developed and is today commercially available under the trademark Nanorestore®. Since then, the scientific research about nanolime and consolidation materials have been evolved, investigating other synthetic strategies with consequent development of other commercial products. As an example, in 2006 nanolimes were synthesized using an alkoxide route and after extensive testing they have been commercialized since 2010 by IBZ-Salzchemie GmbH & Co. KG (Germany) with the trade name of CaLoSil®(Drdácký, Slížková, and Ziegenbalg 2009). Besides nanolime, barium hydroxide nanoparticles, $Ba(OH)_2$ NPs, have been used as a consolidant for carbonaceous materials. More specifically, its use is recommended when large amounts of sulphates are present in a wall painting matrix (Piero Baglioni et al. 2013). Finally, some alkaline earth metal oxide NPs could be useful also for antimicrobial applications. For this purpose, Sierra-Fernandez and colleagues evaluated antifungal properties of magnesium oxide nanoparticles (MgONPs), showing a successful inhibition of the growth of fungi *Aspergillus niger* and *Penicillium oxalicum* (Sierra-Fernandez et al. 2017). In particular, they tested the aforementioned nanostructures on two stone manufacts, the *Laspra* dolostone (Asturias, Spain) and *conchuela* limestone (Yucatán, México), differing in porosity and mineralogical composition, and underlined that the different pore size affected both the fungi proliferation and the active nanostructures distribution. The antimicrobial activity of MgONPs was tested also for paper manufacts. Castillo and colleagues (Castillo et al. 2019) demonstrated their efficacy for the protection of a variety of 18^{th} century papers from the Archives of the Real *Jardín Botánico* in Madrid (Spain) from microbial contamination. The proposed methodology consisted of the coverage of paper surfaces by an homogenous nanoparticle film which did not alter the aesthetics of the paper.

Metal and metal oxide NPs

Apart from alkaline earth metal hydroxide and oxide NPs, the use of metal and metal oxide NPs in the Cultural Heritage field is involved, as well. One of the first causes of the stone artifact damage is the atmospheric pollution. Today, the concentration of pollutants is significantly high in big cities and industrial environments, producing visible stains on buildings. Specifically, small particles and greasy deposits with organic binders such as hydrocarbons and fatty acids (Luna et al. 2018) adhere to building surfaces, thus promoting a significant change in the aesthetic of historic and modern buildings. Different semiconductor metal oxides, such as titanium dioxide and silicon dioxide, were employed in the self-cleaning treatments for cultural heritage stone surfaces. Silica nanoparticles (SiO_2NPs) are used in order to enhance the hydrophobicity of stone coatings. They are usually dispersed in commercial water soluble siloxane emulsion, demonstrating super hydrophobicity, chemical resistance, self-cleaning, anti-fouling, stain-resistance and ice-repellence (Mosquera, Carrascosa, and Badreldin 2018; Chatzigrigoriou, Manoudis, and Karapanagiotis 2013). Titanium dioxide is a semiconductor characterized by long term stability and UV photoactivity, ensuring antibacterial and antifungal abilities due to the production of reactive redox species. In fact, it generates hydroxyl radicals ($OH^\bullet$), superoxide anions ($O_2^{-\bullet}$), and hydrogen peroxide molecules (H_2O_2) which damage cell membrane, inactivating a wide range of organisms. Gherardi and colleagues (Gherardi et al. 2016) demonstrated that titania nanoparticles (TiO_2NPs) dispersion presented a good aesthetical compatibility on *Carrara* marble and *Noto* stone ensuring maintenance and conservation of stone surfaces. However, the stone porosity significantly affected the nanostructure efficacy. In fact, they observed that TiO_2 treatments did not create continuous films on *Noto* stone samples, leading to nanoparticle aggregation into the pores, thus reducing the photoactivity of the samples. On the other hand, TiO_2 photoactivity can be also improved using nanostructured noble metals, such as silver and gold nanoparticles. In fact, the metal nanoparticles in contact with TiO_2 act as electron reservoirs, reducing the recombination of electron-hole pairs. They also have a high localised surface plasmon resonance (LSPR), responsible for several effects, such as, generation of electron-hole pairs, local heating, or increase of the surrounding electric field, which can promote the TiO_2 photoactivity. For example, Luna and co-workers (Luna et al. 2018) demonstrated the use of AuNPs to improve TiO_2 photoactivity in coatings applied on buildings. The biocidal properties of TiO_2 nanostructures was also explored directly treating the southeast wall of *Villa dei Papiri* in Ercolano, Italy (Ruffolo et al. 2017). In this study, the TiO_2 efficacy was tested for more than eight months. The results showed that the TiO_2NPs not only ensured a satisfactory antimicrobial activity, but also they provided the inhibition of re-colonization of fungi and bacteria on the stone surface. Beside TiO_2, the antimicrobial activity of NPs such as silver (AgNPs), copper (CuNPs) and zinc oxide (ZnONPs), has also been considered to fight the natural formation of biofilm on the artwork surface, owing to bacteria proliferation and climatic factors, and prevent the biodeterioration. AgNPs are one of the most effective biocide agents and are widely employed in different fields such as medicine, cosmetics, textile and food packaging industries. The antimicrobial mechanisms of AgNPs is attributed to complex processes related to the inhibition of the protein synthesis and DNA replication, as well as the deterioration of the bacterial cell wall and the plasma membrane (Sportelli, Picca, and Cioffi 2014). The antimicrobial activity of AgNPs is also exploited in the artwork protection and against their biodeterioration. For example, AgNPs were applied against fungi and bacteria that are considered as biodeteriogens of cultural heritage, especially of stone-based monuments (Carrillo-González et al. 2016). They were isolated from aesthetically damaged archaeological walls of a pre-Hispanic city of Teotihuacan, the Citadel. The results of this study showed that AgNPs exhibited broad-spectrum activity against bacteria and fungi associated with the deterioration of these archaeological walls. It was proven that the use of AgNPs as antimicrobial agents is preferred, in comparison with different Ag compounds (-nitrate, -sulfadiazine, -zeolite, -powder, -oxide, -chloride and - cadmium powder). In fact, the antimicrobial action of these compounds on materials under treatment is essentially based on silver ions, whereas AgNPs can act also through contact and ensure high ion release thanks to their high surface area (Maiti et al. 2014). In our laboratories we constantly work on the development of antimicrobial metal and metal oxide nanostructures and coatings. The activity of these nanostructures is typically associated to the release of metal ions, with the consequent reactive oxygen species formation at NP surface (Sportelli, Picca, and Cioffi 2014). The synthesis of NPs is typically performed by electrochemical approaches based on the sacrificial anode electrolysis method (Izzi et al. 2020). In the early work, CuNPs were proposed as antimicrobial nanophases for stone protection (Ditaranto et al. 2011). However, some limitations emerged because of the use of organic solvent for their preparation and, more critically, the resulting brownish appearance of their colloidal solution, associated to plasmonic copper. For this reason, the application of plasmonic NPs on stone surface should be performed with attention (Pinna, Salvadori, and Galeotti 2012). More recently, ZnONPs were synthesized in aqueous solution through a green electrochemical-thermal approach resulting in a white power that could cause in principle less problems in terms of artwork appearance. The nanostructures were produced in the presence of different type of surfactants. According to their nature, several size and morphologies of ZnO nanostructures were obtained, as shown in Fig. 2.

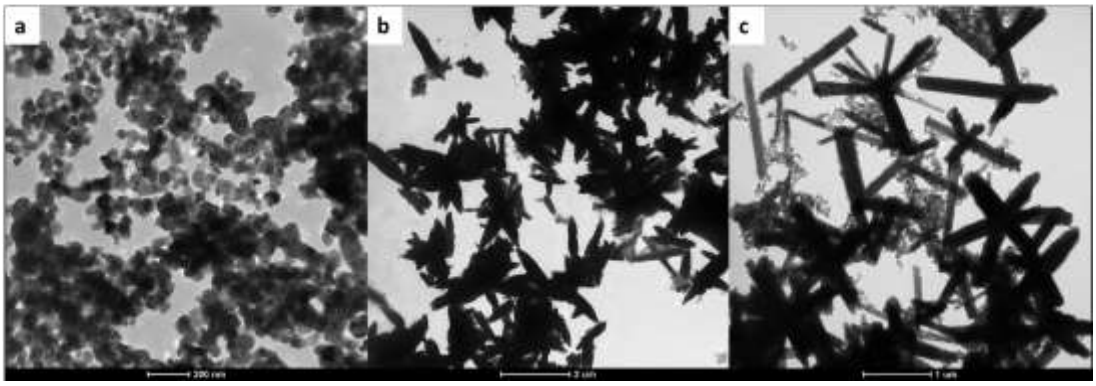

Figure 2: ZnONPs synthesized in the presence of PSS (a), CTAB (b), BAC (c).

For example, spheroidal NPs with an average diameter of 46 ± 8 nm (Picca et al. 2015) were obtained in the presence of an anionic stabilizer, poly(sodium 4-styrenesulfonate, PSS), as shown in Fig. 2a. Alternatively, using a cation stabilizer as cetyltrimethylammonium bromide (CTAB), rod-like structures were formed (Picca et al. 2017). In particular, it was found that elongated ZnO submicrometer rice-grain structures (with length < 2 µm and width < 200 nm, Fig. 2b) could be obtained preparing the colloids at 80°C, and calcining them at 300°C. Finally, their further assembly resulted in cross-like or flower-like aggregates. Similar results were obtained using another asymmetric quaternary ammonium salt as cationic stabilizer, the benzyl-hexadecyl-dimetylammonium chloride (BAC, Fig. 2c) (Sportelli et al. 2020).

The as-synthesized ZnO nanostructures were tested as NPs-based biocides for conservation of stone artworks. In particular, ZnONPs were embedded in consolidant/water repellent matrices to obtain nanostructured coatings. Commonly used tetraethoxysilane (TEOS)- and/or siloxanes- based materials

(Estel1000, Silo111, and Estel1100) were selected to develop antimicrobial consolidant coatings against stone biodeterioration. The developed coatings were tested on three types of Italian stone, from the Apulia region: the *Calcare di Altamura*, *Calcarenite di Gravina* from Massafra, and *Calcarenite di Gravina* from Gravina, demonstrating good ZnONPs penetration, especially for Silo111 coatings, and a successful inhibition of the growth of *Aspergillus niger*, already at low NP concentrations (Ditaranto et al. 2015; van der Werf et al. 2015). A comparative study was performed also with similar coatings embedding CuNPs, demonstrating a similar efficacy. All the proposed coatings were applied on the external part of the apse of the 12th-century church of San Leonardo di Siponto (Manfredonia, Italy). Treatments based on ZnONPs were preferred because of their limited chromatic variations.

3. FUTURE CHALLENGES AND CONCLUSIONS

The unique properties of nanoscale materials enable promising applications in Cultural Heritage. The commercial production of some of them and their good performance encourage the current scientific research on this topic. In particular, some nanostructures usually used in the sensing field, such as graphene and carbon nanotubes, have been tested as nano-reinforcement (Dimou et al. 2020), demonstrating a significantly enhancement of flexural strength. Another suitable way is the development of hybrid (nano)materials that are able to combine two or more properties. In such direction, calcium zincate nanostructures ($Ca(Zn(OH)_3)_2 \cdot 2H_2O$) have been proposed (Soria-Castro et al. 2019; Zagada-Dominguez et al. 2020; Gómez-Ortíz et al. 2013; Ambrosi et al. 2001), in order to benefit from both consolidation properties of calcium compounds and antimicrobial activity of zinc (II) species. The nanocomposite coatings demonstrated a good consolidation ability, as well as an excellent antifungal activity, inhibiting the growth of *Penicillium oxalicum* and *Aspergillus niger*. Hybrid nanomaterials were used for their protection properties. Becerra and colleagues proposed the decoration of $Ca(OH)_2$ Nanorestore® with ZnO dots (Javier Becerra et al. 2019), in order to investigate the real nanolime penetration through stone matrices, exploiting the fluorescence of ZnO quantum dots. As other previous results, the best solubility and kinetic stability were obtained with alcoholic solvents. In addition, it was proven that the ZnO dots remained on the nanolime surfaces without increasing in average size and showed a great fluorescence in the visible region under UV irradiation. This method allows to explore the penetration depth. In our laboratories we are currently following similar strategies to develop innovative smart (nano)coatings of potential application for stone protection. In this scenario, we are developing an innovative one-step synthesis to produce $Ca(OH)_2$-ZnO nanostructures, combining the aforementioned aqueous electrosynthesis of ZnONPs and a wet chemical synthesis of $Ca(OH)_2$.

In this contribution we have highlighted the importance of innovative materials development for the conservation and preservation of movable and immovable artworks. The proposed nanostructures can play a crucial role in this field. However, careful evaluation of novel materials in long-term studies (possibly carried out also on works of art) has to be undertaken before considering them suitable for correct preservation.

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The marble façade of the Ducal Palace of Vila Viçosa in the context of the 1940 Centenary Commemorations: cleaning and consolidation

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SUMMARY:

The main goal of the present article is to study the cleaning and consolidation of the marble façade of the Ducal Palace of Vila Viçosa during the 1940s. The research was based on the archival documentation of the former Directorate-General for National Buildings and Monuments (DGEMN), which was crucial for uncovering the history and theory of conservation and restoration of monuments in Portugal since 1929, and allowed to identify protagonists as well as techniques, materials, and intervention criteria.

The analysis of the choices that were made — based on principles such as minimal intervention, respect for the history of the monument through its various phases, and preservation of the patina of time — demonstrates that there was an obvious regard for the principles established by the Athens Charter (1931). Such principles are evidence of a departure from the DGEMN action paradigms at the time, which favoured restoration over conservation and defended the prevalence of a "style unity", while sacrificing certain eras of the monuments' past.

KEY-WORDS: Monuments; Stone; Cleaning; Consolidation; Archival documentation

1. INTRODUCTION

The Ducal Palace of Vila Viçosa, headquarters of the Most Serene House of Braganza, which ruled Portugal between 1640 and 1910, is one of the most notable group of 16th century manor houses still existing in the Iberian Peninsula today (Serrão 2015, 85-89; Serrão 2018, 135,137).

The several specialists who have studied it (e.g. Teixeira 1983; Moreira 1997; Serrão 2015, 2018; Hallet and Senos, 2018) have contributed significant information on the building—a classified National Monument since 1970 [1]—, on the several stages of its construction, and on its artistic features (mural paintings, carvings, azulejo panels). This article will focus on its magnificent façade, which is completely covered with marble from the Estremoz Anticline.

In 1940, Vila Viçosa was chosen as the setting for the Commemorations of the Centenaries of the Foundation of Portugal (1140) and of the Restoration of Independence (1640), with the impressive façade serving as a backdrop for the celebrations which would take place on the adjacent square. Within this context, in addition to some conservation and restoration works on the building, the DGEMN technicians argued for the cleaning and "repair" of the stonework of the main façade, including the replacement of some broken pieces.

The compelling technical description written on the occasion and the report of the Superior Council for Public Works (CSOP), both unusually detailed documents for the time, establish the action criteria for: The cleaning of the stonework; the consolidation of the joints; and the replacement of stones.

At the time, the interventions on monuments were, in accordance with the guidelines established by DGEMN, mostly aligned with the principle of "style unity" defended in the 19th century by the French architect Eugène Viollet-le-Duc, which led to somewhat radical restorations that sought to retrieve the "original beauty" of the buildings. This makes the approach adopted in this specific case even more surprising, since it complies with the core principles of the 1931 Athens Charter for the Restoration of Historic Monuments, which privilege conservation over restoration and favour the use of ancient materials and techniques over modern ones.

Through the historical study of this National Monument and World Heritage candidate (Vila Viçosa municipality 2020), and specifically of its intervention led by the architect Raul Lino, the goal of this article is to contribute to the debate on the topics of stone cleaning and consolidation (regarding methods, materials, criteria). Investigating past interventions through the listing and analysis of archival documentation not only enriches the knowledge about historical procedures, but also provides insightful information for the understanding of certain patinas or deterioration phenomena now occurring on the materials of monument buildings (Aires-Barros et al. 2006, 89-101).

2. THE MARBLE FAÇADE OF THE DUCAL PALACE

Three storeys high, with 23 sections covered in marble, and with a total length of 110 metres, the palatial façade dates back to the enlargement and monumentalisation of the ducal residence which, according to some authors, was carried out during the reign of Dom Teodósio I, between 1532/1533 and 1563, following the renaissance taste (e.g. Moreira 1997, 48-53); other authors (Senos 2018, 109-134) argue that it dates to the period between the last quarter of the 16th century and the beginning of the following century and that it displays an obvious adherence to mannerist aesthetics [Fig.1].

Figure 1. *Vila Viçosa. Royal Palace*, (c.1900). Secretariado Nacional de Informação, Arquivo Fotográfico, Documental, XII-1, doc. 00829. PT/TT/SNI/ARQF/DO-012-001/00829. Arquivo Nacional da Torre do Tombo (ANTT).

Regardless of the disagreements concerning the exact time period and authors of its construction, the façade has nonetheless an imposing appearance and produces a powerful theatrical effect, showcasing the erudition underlying the architectural project. The construction scheme and the employed materials, especially the marble frontispiece which alternates white and Ruivina marbles from the Estremoz Anticline, are worthy of highlight, and make the Ducal Palace an adequate setting for the political ambitions of the House of Braganza.

The third floor of the marble façade, in the upper part of the central section, also known as "Casa dos Alfaiates" [Tailors' house], was added during the reign of Dona Maria I (i.e. between 1777 and 1816) according to most authors (e.g. D'Arnoso 1904, [4]; Teixeira 1983, 106). This mansard was added as part of a sparsely documented series of construction works and features "three windows with sill and a plaster front with faux marbling" (Cabral 1889, 28) [2].

3. THE COMMEMORATIONS OF THE 1940 CENTENARIES IN VILA VIÇOSA

In Vila Viçosa, the 1940 commemorations of the centenaries focused on celebrating the 1640 Restoration of Independence that put an end to 60 years of Iberian Union, and on celebrating Dom João IV, Restorer of Independence and founder of the new Braganza dynasty (Salazar 2015, 363) [Fig. 2].

Figure 2. *The Council President together with the members of the Commission in charge of celebrating the commemorations of the Centenaries and of the Portuguese Restoration of Independence*. 1938-04-11. Among the pictured, one can identify: Pardal Monteiro; António de Oliveira Salazar; Duarte Pacheco; Raul Lino. Empresa Pública Jornal *O Século*, Álbuns Gerais no. 53, doc. 1155M. PT/TT/EPJS/SF/001-001/0053/1155M. ANTT.

Thus it was announced that "On the square opposite [to the Palace of the Dukes of Braganza, in Vila Viçosa], once it was properly repaired and embellished, one should erect a statue of Dom João IV. The Palace, the vast square, the charming church opposite to Agostinhos, the pantheon of the House of Braganza, would thus be restored to the beauty and dignity that they warrant" (Salazar 2015, 364) [Fig. 3]. Some restoration procedures were also planned for the palace, among them the cleaning and consolidation of the main marble façade.

According to the official program of the celebrations, after the visit, on 15 and 16 November, to some historical sites in Alentejo (Évora, Borba, Ameixial, Fronteira, Elvas), the events planned for Sunday 17 November would include the "Inauguration of the equestrian statue of Dom João IV on the square of the Vila Viçosa Palace. Historical military parade. Tours evoking the Braganza ducal ancestry: the armoury hall of the castle; the Dukes' hall; the Agostinhos and Santa Clara pantheon churches" [*Revista dos Centenários* 15, 18).

Figure 3. Untitled [Vila Viçosa], undated, cota 05524.001.004. Fundação Mário Soares / DTC - Documentos Mário e Alice Chicó - Sílvia Chicó.

As will be further described in the following paragraphs, there were several circumstances that led the commemorations in Vila Viçosa to fall below the expectations, with the Ducal Palace being omitted from the celebrations due to its bad state of conservation and to the postponement of the planned interventions. As for the monument in honour of Dom João IV, created by the sculptor Francisco Franco and the architect Porfírio Pardal Monteiro, it would only be inaugurated in 1943 (Soares et al. 2019, 191-201).

The conservation and restoration of the Palace: proposal for an intervention on the façade

On 6 May 1938, the engineer Henrique Gomes da Silva, director general of DGEMN, issues a request for the Director of National Monuments, the architect Baltazar da Silva Castro, to plan and budget, in collaboration with the Directorate of the Buildings of the South, the restoration works of the Vila Viçosa Palace, which should be concluded in time for the 1940 commemorations [3]. [Fig. 4]

More than a year later, on 25 August 1939, Baltazar de Castro sent Gomes da Silva the project and the estimated cost of the "necessary works for the Vila Viçosa Palace" amounting to a total of 1,799,300$00—808,000$00 of which were allocated for materials and 991,300$00 for labour. The file was sent to the office of the Minister of Public Works, Duarte Pacheco, on the following day [4].

The technical description was written by the architect Martinho Humberto dos Reis, who worked in the third section of the Directorate of National Monuments (southern region) of DGEMN (Neto 2001, 227). According to the document, the intervention consisted almost completely of conservation procedures [5], namely, the dismantlement and reconstruction of the roof framing and covering; paving of the cloister floor with marble from the local region; construction and installation of new chestnut doors in some of the ground floor rooms; general repair of all interior doors, shutters, and frames, including the replacement of broken hardware and glass panes; "renailing" of the floorboards and "replacement of unsafe beams"; general repair of brick pavements or installation of new pavement when necessary; consolidation of brick vaults; laying of marble tiles in the chapel; laying of Mourão tiles, similar to the preexisting ones, in the ground floor corridor; sealing of terraces; plastering of walls and ceilings; general whitewashing of walls and vaults; laying of 16th century azulejos in some rooms of the *piano nobile* (Salema 2020, 121); painting of wood parts and waxing of the chestnut ceilings; restoration of old paintings on wood, canvas, and of murals; electrification of the whole building; repair of the existing lavatories.

Figure 4. *Vila Viçosa. Ducal Palace*, [19--]. Secretariado Nacional de Informação, Arquivo Fotográfico, Documental XII-1, doc. 01129. PT-TT-SNI-ARQF-DO-012-001-01129_m0001. ANTT.

Figure 5. *Vila Viçosa. Palace. Partial view*, [19--]. Secretariado Nacional de Informação, Arquivo Fotográfico, Documental, XII-1, doc. 01058. PT-TT-SNI-ARQF-DO-012-001-01058_m0001. ANTT.

Among the restoration procedures listed on the document, there are interventions on the capitals, columns and vault decorations of some of the halls on the ground floor; and the demolition of walls "of a later construction date" so as to restore some of the rooms to their "original state", and to allow for greater visual continuity and prominence of the vault decorations.

There was also a plan for the construction of a new structure, in one of the outermost sides of the palace, and on preexisting foundations, meant to aggregate several services and storage rooms. As for the façade, the document proposed the "cleaning and repair of the stonework of the main façade, including the replacement of broken marble slabs, in order to display the contrasting colours of the marble which are barely visible today due to the thick patina that, with time, has accumulated there." [Figs. 5 and 6]

Figure 6. Ducal Palace of Vila Viçosa. Partial view of the main façade, [1943]. DGPC/SIPA. 00163278.

The project and budget for the works on the Palace of Vila Viçosa are evaluated, on 31 August 1939, by a commission composed by the DGEMN director general, Henrique Gomes da Silva, and by two engineers of the same institution, as stipulated by the Decree no. 19,881 of 22 May 1931 (*Diário do Governo*, 1st Series, no. 135, 12-06-1931, 1141-1142). The commission confirmed the "accuracy and exact adaptability of the listed procedures to their designated purpose"[6].

In accordance with the aforementioned document, a request for assessment to the Superior Council for Public Works (CSOP)[7] ensues on 29 September 1939. The council produces a document, dated 30 January 1940 and approved by the minister Duarte Pacheco on 10 February, declaring that, in general, the conservation and restoration works on the Vila Viçosa Palace "are apt for approval" [8].

However, the assessment points out that "Of all the procedures mentioned in the technical description there is one which must be examined by the authors of the project", and which concerns the "cleaning and repair of the stonework of the main façade". In regard to this, some interesting recommendations are offered—which will be addressed in the following paragraphs [9].

Recommendations for the "cleaning and repair" of the stonework

The meeting in which the CSOP's assessment of the works on the Ducal Palace of Vila Viçosa was produced was attended by—in addition to the president of the Council, the engineer Raul da Costa Couvreur—the members Francisco Maria Henriques, Luiz da Costa Amorim, Francisco Augusto Homem da Silveira Sampaio de Almeida e Melo, António Vicente Ferreira, Fernando Galvão Jácome de Castro (an engineer representing the director general of National Buildings and Monuments), and the architect Carlos Chambers Ramos.

The meeting resulted in particularly relevant guidelines on the issue of the "cleaning and repair" of the stonework. One very detailed document, unusual for the documentation of the time, grants special relevance to the issue of patina—a debate which, having begun with the anti-restoration movements of the 19th century, would be fomented by Cesare Brandi and by the "critical restoration" movement in the 20th century (Brandi 2006, 107-109) [10].

In an accusatory tone towards interventions made on other monuments, CSOP stated that "frequently one witnesses cleaning procedures of ancient monuments or buildings that go as far as to completely suppress the distinctiveness which only the passage of time can confer". Thus a topic which had already been debated at the Superior Council of National Monuments in the beginning of the 20th century was retrieved [11]. At that time, cleaning procedures that involved scraping and bleaching the stone, instead of relying only on water, had damaged many patinas [12].

Additionally, CSOP highlighted the fact that "The Palace of Vila Viçosa, as it can be seen today, displays an interesting colour due to its golden patina, which must not, under any circumstances, be eliminated".

With regard to this, a crucial distinction between patina and dirt must be drawn and taken into consideration in determining the cleaning procedures: "We must differentiate between the magnificent patina of time and the dirt which has accumulated over the years". Thus, in practical terms, "If it is unavoidable to replace some of the marble slabs of the broken façades (sic), one should not seek to restore the older ones to the brightness of the most recent ones only to reinstate the original contrasts of colour; on the contrary, one should aim for the new marbles to resemble, as much as possible, the colour and appearance of the old ones after having been previously and briefly cleaned."

Such restrained cleaning aiming to preserve the patina of time "should not", according to the assessment by CSOP, "involve the use of grinding wheels nor wire brushes, but only common water and piassava brushes along with the pointer trowels indispensable for clearing the joints and extracting the plants and thick dirt accumulated in the corners, which are quite detrimental to the conservation of buildings".

Regarding the rest of the planned procedures, it is concluded that "all of them are necessary and abide by a general principle of admirable economy and aesthetic sensibility, not falling into exaggerations which often raise the cost of this kind of work" [13].

It is precisely the cleaning and repair procedures of the main façade stonework of the Ducal Palace that CSOP points out as exaggerated. Despite the vague technical description regarding the chosen methods and products, the expressed purpose of revealing the contrasts of the marble covered by the thick patina left by the passage of time reveals the intention of deep cleaning the whole façade, thus likely erasing the marks of authenticity naturally bestowed by time. One can suppose that there was a plan to clean the stonework with hard-bristled brushes and detergent products, as later happened with the National Pantheon in the years between 1950 and 1960. In this monument, in Lisbon, the procedures also included the mechanical cleaning of vaults and archways with polishing machines, so as to clean the joints more thoroughly [14].

In the Palace of Vila Viçosa, the CSOP experts recommended the use of brushes with softer bristles instead of wire brushes, and the use of water as solvent, without the addition of any chemical products [15], and presumably without the use of water jets [16]. This was perhaps a sign that, in Portugal, something was changing regarding the cleaning procedures of the stone in monuments, with the adoption of less radical—but also less "normalised"— approaches (Rodrigues and Charola 2006, 115) which were better suited to the historical value of monuments. Such had already been the case in the façade of the main portal of the Jerónimos church (1935), in which there was a concern for the preservation of the "natural patina left by the passage of time" (Soares 2019, 475, note 213), and would also be the case in the Dom Manuel Palace, in Évora, in which the preservation of the "acquired natural patina" was also considered (1942) [17].

The CSOP's assessment also noted the importance of handling the stonework joints by removing any accumulated plants and dirt which could have gathered there (since the area opposite to the building remained unpaved until 1963) with the use of "pointer trowels"; as well as by resealing the joints with a grout made of hydraulic lime and sand, similar to the preexisting one, as is still recommended in the rehabilitation of historical buildings today (e.g. Veiga and Santos 2015, 38-40). There is no reference to any kind of biocide meant to curb the rapid growth of new live organisms nor to any other kind of chemical product, such as the injections of diluted sulphuric acid which Luiz Mousinho de Albuquerque claims to have used in the Batalha Monastery during the 1840s in order to eradicate the roots of the bushes growing within the stonework joints (Albuquerque 1854, 20, 24); or the "acids diluted in water" which were controversially applied with similar purposes in Rambois' and Cinatti's (1871) cleaning of the stones of the southern façade of the Jerónimos Monastery (Soares 2019, 395). Perhaps it was considered that eliminating the causes of the infiltrations by sealing the joints with grout was enough to significantly decrease the growth of undesirable organisms on the façade.

If it was carried out, the consolidation of the stone with the purpose of restoring its cohesion and adherence was probably achieved through injections of fluid grouts (Luso and Lourenço 2014), as seems to have been common practice in most of the interventions made by DGEMN, at least until 1952. Despite there being a "soluble silica" in the consolidation of the cloister vaults of the Jerónimos Monastery—presumably from an intervention from the beginning of the 20th century (Aires-Barros et al. 2006, 93)—, the use of "Silexore" (silicone) by DGEMN was only identified as dating back to 1952 [18], when it was used on the lateral altars (from the 16th century) of the São Vicente Church in Abrantes (Pamplona et al. 2007, 14-15) and on the plastered walls of a room of the Hostel in the Berlenga island, where issues with salt efflorescences seriously challenged the conservation of the building. In both cases, the employment of "Silexore" was admittedly "experimental" [19], and its efficacy is noticed one year after the application, with the handled stonework presenting "less deterioration than the others" and the lime exhibiting a better adherence to the plaster [20]. After this seeming success, there is a plan to extend the procedure to all the remaining walls of the Berlengas fort of São João Baptista, and eventually to other monuments as well, despite the awareness that "it is still too early to reach any proper conclusion, since any silicate applied under the same circumstances would have lasted at least as long as the Silexore has". Thus, the technical division of the Monuments Service at DGEMN recommends "waiting for a longer experimental period" in order to better assess the product's efficacy [21]. The prudence of the DGEMN technicians regarding the expanding use of a sealant still in its experimental phase is noteworthy. The establishment of effective treatments for stone consolidation remains a somewhat controversial research topic under debate to this day, with examples from the past testifying detrimental consequences for heritage (Rodrigues 2010).

The documents do not mention anything specific regarding the installation of the new stones meant to replace the missing parts of the façade of the Ducal Palace. However, considering the customary practice at that time and the serious concern expressed by the Administration of the House of Braganza Foundation regarding the possible detachment of the stones, a strong plaster made of cement and sand was presumably used, along with, perhaps, rustless brass (of bronze or galvanised iron) "staples" (Costa ca. 1955, 2). These had been used in the construction of the National Pantheon [22] with the purpose of attaching each piece to another and to the wall, and on the main portal of the Jerónimos church (Soares 2019, 409) in order to ensure its stability.

Figure 7. *The Head of State upon his arrival to the Square of the Vila Viçosa Palace* [the façade of the Ducal Palace prior to the intervention], 1943-12-08. Empresa Pública Jornal *O Século*. Álbuns Gerais no. 89, doc. 2304R. PT/TT/EPJS/SF/001-001/0089/2304R. ANTT.

In addition to a preference for new stones harvested in the region, with characteristics similar to the preexisting ones', it is possible that the new marble slabs were waxed, after having been cleaned and consolidated, in order to resemble the older ones in colour and appearance. Such was a usual practice, as it attenuated the contrast with the older marble stones while offering some water-repellent protection.

Regarding the crucial waterproofing of the terraces of the building, which had direct consequences on its general state of conservation, there was a reference, in the documents, to a "water-repellent sealing…, in accordance with the method of the region". This suggests that the employed procedures were different from the ones used in other parts of the country, perhaps due to the climate and the availability of materials, which could not be clarified.

Despite being one of the priorities in the program of the celebrations of the centenaries, and of the speed with which the technical and administrative process regarding the intervention on the Palace was handled, the truth is the actual intervention, led by the architect Raul Lino, only began after the 1940 celebrations, after the Administrative Board of the House of Braganza Foundation took office in January 1945 (Monge 2017, 18, 20). [Fig. 7]

The execution of the intervention on the palace building

One of the major causes for the delay of the works planned for the Palace of Vila Viçosa was probably the fact that the palace did not belong to the State, which led to difficulties in the communication between the parties involved in financing and executing the work. In addition to this, the time for the execution was tight, and there was a general shortage of specialised labour and materials due to the the World War II.

The decree-law no. 33,726 of 21 June 1944 would prove to be fundamental for the beginning of the intervention on the Vila Viçosa monument. This diploma established that the House of Braganza Foundation held the usufruct of the estate left by Dom Manuel II, which included the Palace of Vila Viçosa, and it assured a loan from Caixa Geral de Depósitos (the state-owned bank) with the State acting as a guarantor. The loan was meant to pay for the "considerable repair works" necessary in the Palace buildings, as well as for the establishment of the Museum-Library. Until then, the estate left by the last Portuguese monarch had been held by Queen Dona Amélia, his mother, and by Queen Augusta Vitória, his wife.

The process was set off by the notice issued by the president of the new administrative board of the House of Braganza Foundation, António Luís Gomes (who was also director general of the National Treasury), dated 23 February 1945 and addressed to the general director of the National Buildings and Monuments, engineer Henrique Gomes da Silva. In the notice, the board expressed an interest in "starting the preparatory works for the establishment of the Museum-Library in the Ducal Palace of Vila Viçosa as soon as possible" [23].

The following procedures included the project location and the budget for the conservation and restoration works needed in the Vila Viçosa monument—both prepared by DGEMN in 1939—, with copies being sent to the administrative board of the foundation. The elaboration of a new project with an updated budget, in November 1945, was based on these documents. Nevertheless, the works resumed as they had been planned in 1939, as both technical descriptions testify.

From the listed procedures, described as ″almost entirely conservation works"—thus deliberately highlighting the scarce number of restoration works—, we consider particularly pertinent to our study:

- the "cleaning and repair of the stonework of the main façade, including the replacement of broken marble slabs, in order to display the contrasting colours of the marbles, which are barely noticeable today due to the thick patina left by the passage of time";
- the paving of the cloister floor with marble stones from the region;
- the replacement of the marble tiles in the chapel.

Other listed procedures—though not all of them were executed (Monge 2017, 68-69)— are also noteworthy, since they clearly reflect the priorities and criteria for the intervention:

- water-repellent sealing of terraces, employing a method local to the region;
- replacement of several wooden doors;
- glassing of windows;
- several repavings "in accordance with the preexisting" pavements and using materials available on site;
- demolition of "several stone walls of a later construction, which currently divide rooms and other areas, in order to restore them to their original state and thus allow for continuity in the decorations of the vaults";
- laying of 16th century azulejos in some rooms of the *piano nobile*;
- restoration of old paintings on wood and canvas, and of several frescos;
- electrification of the whole building [24].

Regarding the total budget for the intervention, the cost more than doubles in 1945 when compared to the 1939 estimate "due to considerable price fluctuations registered since its formulation", as stated by Luís Gomes, president of the administrative board of the foundation, in a letter addressed to the engineer director general of the National Buildings and Monuments [25]. The rise in cost from 1,799,300$00 (808,000$00 allocated for materials and 991,300$00 for labour) to 3,937,300$00 (1,966,200$00 for materials and 1,971,100$00 for labour) was certainly not only caused by the six-year interval between the two estimates, but also by the general inflation in the prices of materials within the context of World War II.

The cleaning and consolidation of the façade (1945)

Raul Lino, then chief architect of the Department for Studies and Works on Monuments of DGEMN (Neto 2001, 226), authored the intervention plan on the Ducal Palace which aimed to adapt the building into a Museum-Library. He also designed various furniture pieces for the interiors, as well as doors, doorknobs, and door locks, and conceived the lighting project for the Terreiro do Paço square opposite to the building. The progression of the works was overseen on site by the military engineer Ricardo Moreira do Amaral, an artillery colonel about whom little could be uncovered. As will be further demonstrated, he would express some disagreements with Raul Lino—as testified by the correspondence he exchanged with the House of Braganza Foundation (Monge 2017, 48)—resulting from different opinions on the action criteria.

From what it was possible to gather from the restricted access to some of the archival documents in Vila Viçosa, the works executed between 1945 and 1953 were essentially the ones necessary for the adaptation of the old Palace to a Museum-Library, but also for salvaging the building from the advanced state of degradation caused by several years of intermittent occupation by the royal family. "The major repair works" seen as necessary in 1938 became fundamental for ensuring the conservation of the building, and included the replacement of window and door frames, the glassing of windows, the repair of the roofs, the cleaning and repair of the stonework of the façade, the application of limewash on various locations, the electrification of some parts of the building, the removal of wallpaper and carpets, the replacement of ceilings and floorboards, and the restoration of mural paintings (Monge 2017, 107 Anexo 2 – Intervenções no edifício entre 1945 e 1948). As for the floor pavement, Lino's plans "for paving the Dukes' Hall with various marbles" are noteworthy, despite the fact that, in practice, such option seems to have turned into a combination of marble and quarry tiles, which a few years later became a floor entirely covered with quarry tiles (Monge 2017, 71).

The intervention on the palace façade, which is of particular interest to the present study, took place in 1945, and was among the first works made on the building. Apparently, it even became a priority, as revealed by the urgency and concern expressed by the administrative board of the foundation in November 1945 to the director general of the National Buildings and Monuments, stating that the board was "extremely" worried "about the state of conservation of the exterior of the Ducal Palace… and will be alert to any immediate need for intervention in order to attach the marble slabs and prevent them from falling" [26]. Accordingly, the works focused on repairing the stonework, specifically on attaching the marble slabs in risk of falling and endangering people, and also on the replacement of some broken elements.

According to the description written by the teacher and writer Sant'Anna Dionísio and published in 1947, the results of the works on the façade seem to not have been very noticeable, since, as he wrote, "The façade is covered with a local marble known as 'bardilho from Montes Claros' [27] (which was installed on the façade in order to embellish it during the 17th and 18th centuries), became strikingly unsightly with time, both at first glance and upon a longer and closer inspection. The most demanding observers should find the brownish and somber (some days, even the same colour as rust and brick) appearance of the façade, caused by the peculiar degradation of said 'bardilho', particularly hideous. The technical imperfections are no less noticeable when one attentively examines the façade. On many interlayering planes and frames, the marble slabs seem to have been crushed, fractured, or neglected. The broken perpendicular axis is particularly visible from the southern side of the façade" (Dionísio 1947, 45-46).

In 1953, in the volume of *A Arte em Portugal* dedicated to Vila Viçosa, Luís Cardim also mentions the "Marble which covers the whole façade, the so-called 'bardilho branco' from Montes Claros [which], with time, has acquired a dark tone" (Cardim 1953, 14). [Fig. 8 and 9]

Figure 8. *Palace of Vila Viçosa and D. João IV statue (by Francisco Franco)*, (c. 1955-1960). Secretariado Nacional de Informação, Arquivo Fotográfico, Panorama, Pastas Geográficas, no. 239, doc. 33. PT-TT-SNI-ARQF-PN-001-239-033_m0001. ANTT.

Such testimonies are perfectly aligned with Raul Lino's criteria for the intervention on the façade, which he made clear by stating that "…we take no interest in plumb lines nor in rigorous alignments, but in ensuring the permanence of what already exists" (AFCB, Correspondência, Raul Lino, report from 7 November 1945. Apud Monge 2017, 74). Furthermore, the DGEMN architect adds: "We find the recommended vigilance of the state of conservation of the Palace exterior of the utmost usefulness, but we believe that, before reaching a conclusion on the distant or recent cause of the mentioned alterations (lest it should recommend a total demolition of the walls, including the foundations, and their subsequent reconstruction!), it would be better advised to proceed by simply attaching them when the need to prevent their falling arises" (AFCB, Correspondência, Raul Lino, report from 7 November 1945. Apud Monge 2017, 74).

Figure 9. *Ducal Palace of Vila Viçosa. Monument to D. João IV on Terreiro do Paço. Sculpture by Francisco Franco*, (c. 1960). Secretariado Nacional de Informação, Arquivo Fotográfico, Documental, XII-1, doc. 73677. PT-TT-SNI-ARQF-DO-012-001-73677_m0001. ANTT.

The dismantling of the mansard located on the axis of the façade main body was considered at this stage. The structure was known as "Casa dos Alfaiates", and was regarded by most authors as a "petty and awkward construction from the end of the 18th century" (Dias [1953]), "disharmonious" and "truly banal", offensive to the "monumental dignity" of the building (Dionísio 1947, 46). However, considering the minimal intervention defended by Raul Lino — which favoured keeping the preexisting structures, as had been done with the 18th-century main chapel in the Lisbon Cathedral (Neto 2002, 262-263) — he must have certainly opposed such demolition.

Intervention criteria: effects of the Athens Charter (1931)?

After the necessary diagnosis of the state of conservation of the building, the principles that prevailed in the works on the Ducal Palace of Vila Viçosa were based in values such as the use of preexisting materials, minimal intervention, and a general respect for the different phases of the monument. In a time when the interventions, following the DGEMN action criteria, were mostly directed at restoring historical buildings back to their "original beauty"—in accordance with Viollet-le-Duc's precept of "style unity" (Neto 2002, 257-261)—, the caution manifested by the CSOP experts becomes even more remarkable, as it favoured the monument's authenticity, defending the soul materialised in the centuries-old golden patina, and thus in line with Raul Lino's approach when he later took charge of the works on the Palace of Vila Viçosa in 1945.

Critical of "style unity", Raul Lino plays an essential part in transforming the practice of conservation and restoration of monuments, as he was — wether intentionally or not—aligned with the most recent international ideas on the subject, namely the ones debated at the International Congress of Architects and Technicians of Historic Monuments (Athens, 1931) (Pereira 2012, 69), which resulted in the first international document on matters of conservation and restoration.

Raul Lino publicly declared his opposition to stylistic restoration in 1941, when, with respect to the Funchal Cathedral (Lino 1941, 5-15), he harshly criticised interventions which, in pursuit of style purity, did not acknowledge the "poetics of the soul" of monuments nor their "picturesque character" materialised in old stonework and its patina (Neto 2001, 236-237). His place as director of the Department for Studies and Works on Monuments, an important role within the DGEMN hierarchy, makes his public criticism of the action criteria for the interventions carried out by that same entity even more perplexing (Neto 2002, 256). His course of architecture studies at the Hannover University, his knowledge of John Ruskin's and William Morris' anti-restoration theories (Neto 2001, 236-238), and some echoes of the ideas on the Athens Charter certainly contribute to justify the ideas he endorsed.

This is the context within which Lino notably opts to respect the preexisting structures and materials, thus positively valuing the building and the historical memory evoked by it, while excluding "radical technical restorations" or imitations that may "be deceiving in regard to the time of their execution" (AFCB, Correspondência, ofício nº 2677/ 14 November 1950. Apud Monge 2017, 53).

In line with the principles defended by the group of CSOP experts led by engineer Raul da Costa Couvreur, Raul Lino declares that "In the present case [Ducal Palace of Vila Viçosa] a special importance was given to the conservation of the appearance of the monument, and, since we know from experience what comes out of complete dismantlement and subsequent reconstructions of the original materials, we prefer to keep the existing constructions at whatever cost. We take no interest in plumb lines nor in rigorous alignments, but in ensuring the permanence of what already exists; we are concerned with preserving its evocative value, which would undoubtedly be erased with a radical technical restoration" (AFCB, Correspondência, ofício nº 2862 / 6 November 1945. Apud Monge 2017, 53).

In turn, the engineer Ricardo Amaral—who, according to Raul Lino, "appears to have a more mathematical sense of monument restoration" (Monge 2017, 54)—manifests his distaste for the architect's "poetic" ideas, and expresses to the president of the administrative board of the House of Braganza Foundation that "It seems (…) that many are led by an ideal of reestablishment to what their heart vaguely envisages as the original form, but I believe there is a danger of going even further back than such form, back to what preceded everything and every shape or form: chaos" (AFCB, Correspondência, 11 February 1949. Apud Monge 2017, 54). This view seems to have been shared by the DGEMN administration, since, in the 1941 report on the Church of Atalaia (Vila Nova da Barquinha, Santarém), a text possibly authored by engineer Henrique Gomes da Silva (Neto 2001, 236) describes certain ideas as naive, full of "soft poetry", with no purpose other than "leaving all of the nation's artistic heritage to crumble, turn into ruins, and be lost forever" (*A Igreja Matriz da Atalaia* 1941).

The prevalence of Raul Lino's ideas, based on minimal intervention principles and on the prioritisation of conservation over restoration, gave way to new possibilities in the realm of monument intervention in Portugal, turning the Palace of Vila Viçosa into a fruitful example. The repurposing of the building into a Museum-Library open to the public ensured "its continuity" while respecting "its historical or artistic character", as recommended in the Athens Charter, thus reinforcing, in our view, the project's alignment with new international trends.

4. FINAL REMARKS

The intention of turning Vila Viçosa into one of the main settings for the 1940 centenary celebrations drew attention to that village in Alentejo during the Estado Novo (Soares et al. 2019).

However, the conservation and restoration works planned for the Ducal Palace, along with other urban interventions, ended up not being executed in time for the commemorations. The fact that the building was not property of the State, added to the several hindrances during the works—mostly due to a shortage of materials and specialised labour, as the world went through a devastating war—are certainly among the main reasons for such delay.

The investment the House of Braganza Foundation made in the Ducal Palace between 1945 and 1953, with the repurposing of the derelict building into a Museum-Library open to the public, contributed decisively for the conservation of an exceptional monument, as well as for the creation of an important cultural and touristic point of interest in the village.

The principles adopted in the intervention—led by architect Raul Lino at the service of DGEMN — are noteworthy, since they were focused on preserving the existing structures and favoured procedures that did not compromise the "soul" of the monument nor its "picturesque character".

The cleaning and consolidation of the palatial façade—the "marble frontispiece", as it was called by Priest Espanca (Espanca 1892, 385) — was executed in 1945 according to those same principles and thus preserving the patina left by time, which explains Sant'Anna Dionísio's description of the "brownish and somber (some days, even the same colour as rust and brick) appearance of the façade", two years later (Dionísio 1947, 45-46).

During the final year of World War II—which promoted some of the most brutal episodes of heritage destruction on a global scale—, Raul Lino aligned his intervention—intentionally or not—with the core principles of the Athens Charter (1931), which privileged conservation over restoration and aimed to "respect the historical and artistic work of the past without erasing the style of any particular period". This helps to explain, for instance, the preservation of the often criticised "Casa dos Alfaiates".

The recommendations issued by CSOP for the "cleaning and repair" of the marble stones, which are contained in a document of the utmost importance to the history of the restoration of monuments in Portugal, are equally noteworthy. They defend the "particular nature" of time, responsible for the "golden patina" on the marble façade, and differentiate between patina and dirt, as is still recommended in current procedures (Rodrigues and Charola 2006, 103-104, 114-115). The former, which "must not, under any circumstances, be eliminated", is seen as a synonym not only for antiquity, but for authenticity. As such, instead of wire brushes or grinding wheels, which are considered too abrasive, CSOP recommends the use of nothing but water and piassava brushes when cleaning the façade. This restrained and cautious approach was the one adopted and followed by Raul Lino, thus proving an appreciation for the value of the monuments and a respect for their history, which is testified by the archival documentation. This frame of mind— present in both CSOP's and Raul Lino's stances—reveals changes in the most radical action paradigms of DGEMN, and, in our view, echoes the Athens Charter.

Following criteria that tend to be less "normalised"—as the ones listed on the charter—, DGEMN seems, through its technicians, to begin to adapt the approach to each specific case, in accordance with the characteristics of the materials, the nature of the existing problems, and the age of the monument, while preserving the patinas of time. This was the case with Vila Viçosa, the Palace of Dom Manuel in Évora, and the main façade of the Jerónimos Monastery, to cite some of the analysed examples; firmer conclusions would naturally require a more representative sampling.

Although the DGEMN documents lack information regarding the products and techniques used until the mid-20th century (Aires-Barros 2007, 14, 16, 19), they nevertheless constitute a vast collection of the utmost importance for the history and theory of monument conservation and restoration in Portugal, allowing to compile information which may become invaluable for the making of informed decisions in present-day interventions.

Endnotes

[1] Cf. Decree no. 251/70, *Diário do Governo*, 1st Series, no. 129, 3-06-1970.

[2] The outside of the "Casa dos Alfaiates" was covered with Ruivina marble in the course of the intervention executed by the company Monumenta in 2009-2011 (Mateus and Claro 2011, 14-15).

[3] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSID-001/007-0815 (Paço Ducal de Vila Viçosa : Processo Administrativo) 06.05.1938, SIPA TXT.00246319. Accessed November 23, 2020. http://www.monumentos.gov.pt/site/app_pagesuser/SIPA.aspx?id=2750.

[4] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0060 (Palácio de Vila Viçosa) and PT DGEMN:DSARH-010/298-0070 (Palácio de Vila Viçosa), SIPA TXT.01928256, SIPA TXT.01928892- TXT.01928894.

[5] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0060 (Palácio de Vila Viçosa) *Memória Descritiva. Obras de Restauro e Conservação do Palácio de Vila Viçosa*, 16.06.1939, SIPA TXT.01928314- TXT.01928311.

[6] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0070 (Palácio de Vila Viçosa) *Parecer da Comissão*, 31.08.1939. SIPA TXT.01928895.

[7] The Superior Council for Public Works, which originated from the General Council for Public Works established in 1852 by Fontes Pereira de Melo, was an advisory technical committee whose goal was to assist the government in the decision-making regarding public works projects. Decree no. 19880/31, *Diário do Governo*, 1st Series, no. 135/1931, 12-06-1931.

[8] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSID-001/007-0815 (Paço Ducal de Vila Viçosa : Processo Administrativo), *Parecer*, fl. 4, SIPA TXT.00246328.

[9] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSID-001/007-0815 (Paço Ducal de Vila Viçosa : Processo Administrativo), *Parecer*, fl. 2, SIPA TXT. 00246330.

[10] The quote was extracted from a text titled "The Cleaning of Pictures in Relation to Patina, Varnish and Glazes", published by Brandi in *The Burlington Magazine*. vol. 91, no. 556 (July 1949): 183-188.

[11] Technical advisory committee created within the Ministry of Public Works working within the context of national monuments. *Diário do Governo* no. 294, 30.12.1898.

[12] ANTT, Academia Nacional de Belas-Artes de Lisboa, Conselho de Monumentos Nacionais, Livro de Atas, (1900-1906) sessão de 15 de março de 1905. PT-ANBA-ANBA-A-001-00015_m0068. Accessed November 28, 2020. https://digitarq.arquivos.pt/viewer?id=4611677.

[13] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSID-001/007-0815 (Paço Ducal de Vila Viçosa : Processo Administrativo) *Parecer*, fl. 3, SIPA TXT.00246329.

[14] 1965, SIPA/ DGPC [DGEMN], Igreja de Santa Engrácia / Panteão Nacional- IPA.00004721. PT DGEMN:DSID-001/011-1287 (Igreja de Santa Engrácia / Panteão Nacional : Obras). Accessed November 23, 2020. http://www.monumentos.gov.pt/site/app_pagesuser/sipa.aspx?id=4721.

[15] The periodical titled *A Construcção Moderna* lists various "recipes" for cleaning marble.

The use of "cream of tartar", caustic soda, or calcium chloride, to which water is added, are some of the suggestions. *A Construcção Moderna*, no. 147 (October 20 1904): 214.

Another recipe meant for removing stains prescribes boiling solutions of soap, soda, blue stone, and water. *A Construcção Moderna*, no. 331 (June 20 1910): 248. To remove "oil stains", the use of a paste made with White Paris granite and benzine or lime chloride is recommended. *A Construcção Moderna*, no. 467 (June 10 1916): 87. The maintenance of the "shine and polish" of the marbles is maintained by applying petrol using a cloth soaked with the substance. *A Construcção Moderna*, no. 462 (March 25 1916): 47.

[16] As an example, we cite the 1871 cleaning of the interiors of the Jerónimos Monastery church, in which brushes were used instead of water jets, since these could endanger the vaults' stability. Centro Cultural Casapiano/Arquivo Histórico da Casa Pia de Lisboa, Serviço Geral, *Officios Recebidos de Diversas Auctoridades* (1864-1873), Caixa 2119.

[17] SIPA/ DGPC [DGEMN], Paço de Évora / Paço de D. Manuel / Palácio de D. Manuel (Évora)- IPA.00001185. PT DGEMN:DSARH-010/092-0113 (Palácio de D. Manuel, em Évora). Accessed December 22, 2020. http://www.monumentos.gov.pt/Site/APP_PagesUser/SIPA.aspx?id=1185.

[18] Note that DGEMN was established in 1929.

[19] There is a mention to a "report of the experiments made with the product 'Silexore'" in S. Vicente de Abrantes. SIPA/ DGPC [DGEMN], Igreja Paroquial de São Vicente / Igreja de S. Vicente (Abrantes)- IPA. 00001986. PT DGEMN:DSID-001/014-1990/2 (Igreja de São Vicente dos Mártires- Processo Administrativo/Obras). Report from 24.09.1953. SIPA TXT.00674073. Accessed December 22, 2020. http://www.monumentos.gov.pt/Site/APP_PagesUser/SIPA.aspx?id=1986.

[20] SIPA/ DGPC [DGEMN], Igreja Paroquial de São Vicente / Igreja de S. Vicente (Abrantes), IPA. 00001986. PT DGEMN:DSID-001/014-1990/2 (Igreja de São Vicente dos Mártires - Processo Administrativo/Obras). Report from 02.06.1954. SIPA TXT.00674080.

[21] SIPA/ DGPC [DGEMN], Igreja Paroquial de São Vicente / Igreja de S. Vicente (Abrantes), IPA. 00001986. PT DGEMN:DSID-001/014-1990/2 (Igreja de São Vicente dos Mártires - Processo Administrativo/Obras). Reports from 13.10.1953 and 02.06.1954. SIPA TXT.00674074.

As regards the intervention made in 1968 on the portal of the Nossa Senhora da Conceição Church, there is a remark on the careful cleaning procedure "with clean water and a soft-bristled brush" and on its consolidation, similar to what had been done 15 years ago in the S. Vicente de Abrantes Church, "by applying two or three coats of 'Silicone' which should harden due to a chemical reaction between the limestone and the silica from the 'Silicone' product, with the absorption occurring on a deep level." This report seems to reinforce the notion that the employment of "Silexore" in the Abrantes church was experimental, remaining a rare practice until at least 1968. SIPA/ DGPC [DGEMN], Igreja da Santa Casa da Misericórdia de Lisboa / Igreja de Nossa Senhora da Conceição Velha, IPA.00006470. PT DGEMN:DSID-001/011-1266 (Igreja da Conceição Velha : Processo Administrativo), Accessed December 22, 2020. http://www.monumentos.gov.pt/site/app_pagesuser/SIPA.aspx?id=6470.

[22] 19-08-1960, SIPA/ DGPC [DGEMN], Igreja de Santa Engrácia / Panteão Nacional, IPA.00004721. *Memória* PT DGEMN:DSID-001/011-1284 (Igreja de Santa Engrácia / Panteão Nacional : Obras).

[23] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0070 (Palácio de Vila Viçosa) , SIPA TXT.01928906.

[24] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0060 (Palácio de Vila Viçosa) *Orçamento – Obras de Restauro e Conservação do Palácio de Vila Viçosa*, 17.05.1939, SIPA TXT. 01928261.

[25] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0070 (Palácio de Vila Viçosa) , report from 25.05.1945. SIPA TXT.01928917.

[26] SIPA/ DGPC [DGEMN], Paço Ducal de Vila Viçosa- IPA.00002750, PT DGEMN:DSARH-010/298-0070 (Palácio de Vila Viçosa), report from 29.11.1945. SIPA TXT.01928918.

[27] A kind of greyish marble from Alentejo. The term 'bardilho' has fallen out of use, and this kind of marble is currently known as Ruivina.

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Chafariz da Glória, Ouro Preto, MG: documentation and characterization of degradation processes for proposing consolidation actions

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SUMMARY: The Chafariz da Glória is one of the many existing fountains in the historic city of Ouro Preto, MG, Brazil, built in the 18th century, with the function of meeting the needs and difficulties of water supply. Listed as National Artistic Heritage in 1950, its main construction material is Itacolomy quartzite, present in its important and decorative elements. This article presents data and preliminary results of a study that investigates the causes and the motivating agents of the degradation suffered by the stone material employed. With this objective, a survey of the current situation of the property was carried out, which resulted in the production of a map that highlights its most important damage. As a starting point, extensive historical and iconographic research was developed, followed by a macroscopic characterization of the stone, as well as a preliminary identification of the degradation and the agents responsible for it. In a near future phase, this study also aims to propose consolidation solutions that may result in less aesthetic intervention and, at the same time, a more durable conservation approach.

KEY-WORDS: Chafariz da Glória, Itacolomy quartzite, stone degradation, Ouro Preto, damage mapping

1. INTRODUCTION

The water fountain named *Chafariz da Glória* (Figure 1) is one of the most important urban elements in the historic city of Ouro Preto, MG, Brazil, having been listed in the Fine Arts book in 1950 (inscription 374, process number 0430-T), and it is located at *Antônio de Albuquerque* street, formerly *Rua da Glória*, which gave it its current name.

According to the portal of the National Institute of Historic and Artistic Heritage (IPHAN, 2020), the Senate of the Chamber of Vila Rica took initiative steps to build the *Chafariz da Glória* by means of public bidding, according to the bidding document dated August 12, 1752, with the objective of supplying water to that region. At that time, the contracting of public works, renovations and maintenance of urban equipment was carried out by the Senate of the Chamber through the publication of a bidding notice, entrusting the services to the bidders, stonemasons and contractors. According to the rules of the bidding, the winner was the one who offered the lowest price and committed their goods or that of their guarantors to complete the work within the time specified in the contract. Thus, the bidders should carry out the work under the guidance of a project and in accordance with the conditions defined by the prevailing power. In the case of fountains, for example, the type of stone to be used, the number of spouts, ways of sealing the pipes and other characteristics were defined in the bidding notice.

Figure 1: *Chafariz da Glória*, Ouro Preto-MG. Source: authors' file, 2020.

Thus, the construction of the *Chafariz da Glória*, known at the time as *Chafariz do Ouro Preto* (Carvalho, 1936), was completed by Antônio Fernandes de Barros and Antônio da Silva Erdeiro, for the sum of 700,000 réis (currency at the time) according to description in Carvalho (1936), translated by us:

> "After bidding process, Antonio Fernandes Barros e Antonio da Silva Erdeiro were in charge of carrying out the construction of *Chafariz do Ouro Preto*; they were the smallest bid, which equaled to seven hundred thousand "reis" (currency of the time), according to the public documentation available." (Carvalho, 1936, p. 113).

However, the authorship of the sketch was not documented. In the auction of the *Chafariz da Glória*, one of the conditions was that the other fountain named *Chafariz do Passo do Antônio Dias*, located in the same name district, should be used as a model, both differing only by the pine cones that flank the pediment. The works continued in accordance with the conditions of the auction and were completed in due time (Carvalho, 1936).

Today, the *Chafariz da Glória* is inactive and it is considered a documentary, historic, and cultural register of Ouro Preto, being an inseparable element of the landscape of the city's enshrined urban ensemble. Over the years, it has undergone several processes of maintenance, conservation, restoration and even some changes. It is essential for proposing long-lasting solutions and permanence of the monument as a cultural record for a longer time, to characterize the construction materials that make up the monument and relate them to the works done on the fountain until today, as well as, to the types of damage it has suffered over the years and their respective agents.

As a result, the research methodology consisted, in a preliminary phase, of bibliographic and iconographic research in order to know the history of the fountain. The research process involved the assessment of the restoration interventions that the fountain has undergone over the years based on photographs from different periods, with analyses of the recurrence of degradation throughout the years. The research also allowed us to obtain information about the extraction area of the stone material used. In the next phase, the mapping and characterization of the degradations were developed, together with the visual identification of possible biological agents through observation of cell culture, among other investigations that were considered necessary. After detailed characterization and documentation of the deterioration patterns, we intend, in a third phase, to find consolidation solutions that will cause the least aesthetic intervention on the fountain and, at the same time, a more lasting conservation solution.

2. URBAN AND ARCHITECTURAL DESCRIPTION

The municipality of Ouro Preto has an average altitude of 1,116 m, presenting a tropical altitude climate, an average rainfall of 2,018 mm / year, with irregular distribution, and rains concentrated in the summer. The average annual temperature is 18 degrees centigrade, generally ranging from 6º C to 28º C, but it can reach 2 º C in June and July (*Prefeitura de Ouro Preto*).

The *Chafariz da Glória* receives insolation throughout the day, in the morning on its east (posterior) facade and in the afternoon on its west (frontal) façade (Figure 2). Regarding afforestation, the back of the fountain has large vegetation of small and large size, which goes up to the slope of *Getúlio Vargas* street. Concerning the relief, it is predominantly mountainous, with many slopes; however, the street where the fountain is located is in the lowest portion of the city.

Figure 2: Incidence of solar radiation at Chafariz da Glória at noon in July (left) and in the afternoon at 4 pm (right). Source: authors' file, 2020

Public lighting along the street is sufficient, with no specific and direct lighting for the monument. The road is paved with polyhedral pavement, with heavy traffic of vehicles and pedestrians during working days, and buses do not circulate on the road. There are no buildings next to the fountain. The surrounding buildings follow the characteristics of the city's urban complex, with the facades aligned with the sidewalk of the streets and without lateral clearances, portraying the characteristic configuration of the urban occupation of the 18th and 19th centuries.

The *Chafariz da Glória* is of the parietal type, in support, embedded in a slope with accentuated global slant that descends from *Getúlio Vargas* street (Downtown) towards *Antônio Albuquerque* street (*Pilar* neighborhood). The back area supported by the retainer is not paved and it is accessed by a paved ramp with rolled pebble. The land is staggered with dry stone retaining walls, and it has characteristics of non-compacted landfill. Surveys carried out in 2010 at *Getúlio Vargas* street indicated a landfill from 3.0 to 5.0 meters deep. There is no drainage system that directs water from the slope, which keeps the terrain moist even in short periods of drought (IGEO, 2015).

The fountain is built centrally on the dry stone masonry wall, which extends along the entire slope, composed of stepped slopes and covered by small, medium and large vegetation. The masonry is covered with stucco made of sand and lime, as well as, and finished with limewash, as required by the Senate of the Chamber (Carvalho, 1936).

According to the *Chafariz*'s bidding document, the bidder should execute the tank and three spouts in *Itacolumy* stone (Carvalho, 1936). The use of the Itacolomi quartzite is evident in all the ornamentation of the fountain stonework. The framing includes side wedges with a stepped base, flat shaft with straight profile, Tuscan capital and right collar, topped by the broken pediment composed of (volutes), architrave, frieze and cornice. Close to the pillars and capitals there is a small spiral scroll under the continuation of the entablature. This whole set is surmounted by pinnacles with a square base, flattened volume and rounded edges. On the card, in the center of the pediment, there is a latin inscription which reads: "Curia Curat, Amatm, Fabricat, Propinat, Abhorret, Libertatem, Stagua, Flu (...) Ta Setim", whose translation is, "The Senate of the Chamber watches over us, loves abundance, makes tanks, provides running water, bores the thirst". (PMOP, 2011). However, it is currently not possible to view the sentence perfectly due to wear in the grooves of the letters.

The three figurehead-shaped spouts (gargoyles) are centered in the central panel, above the tank, under a small cymbal divided into three staggered parts and framed by a thin cornice, with rounded ends. In each gargoyle mouth there is a copper pipe, located above the respective bowl of the tank, in a thick quartzite slab. Finally, the panel is finished off with a shell that overlaps part of the pediment's entablature. The centralized tank is built in stone and lime masonry, covered with mortar and painted in an ocher yellow color (Figure 3).

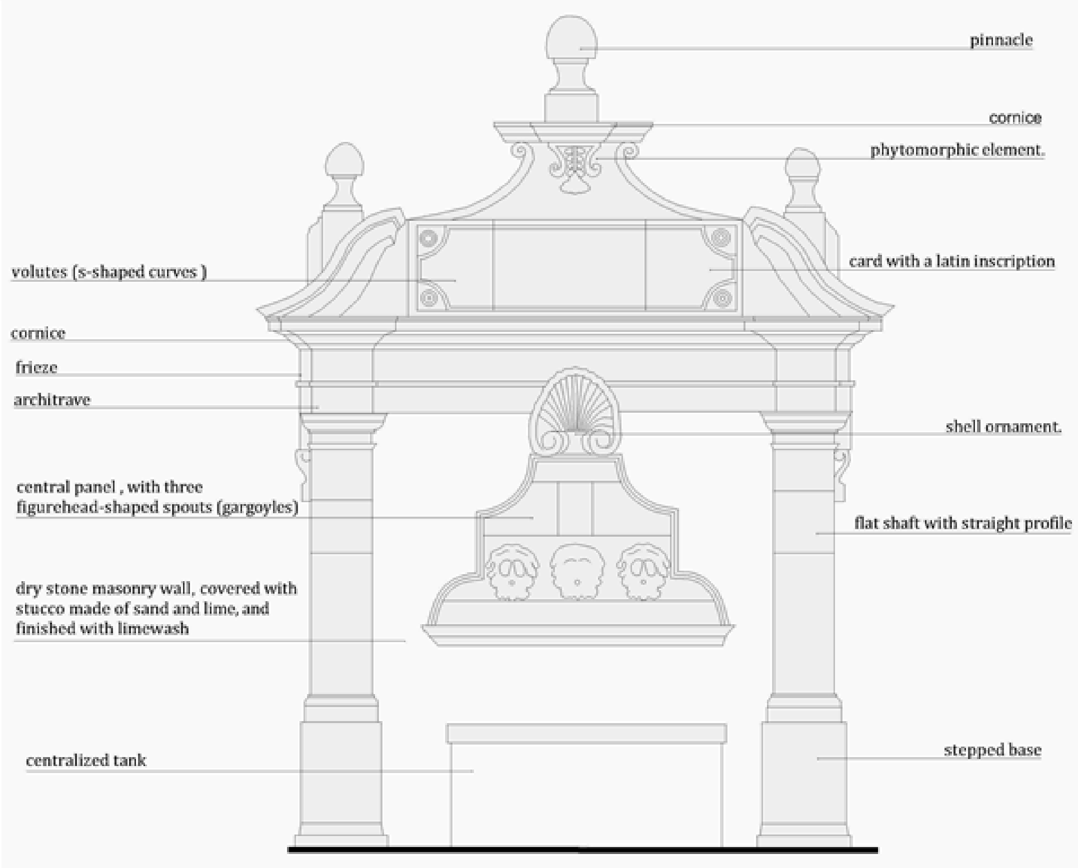


Figure 3: Illustration of the architectural description of *Chafariz da Glória*
Source: authors' file, 2021.

3. STONE CARACTERIZATION

Among the stone materials used in historic mining constructions, local materials have always prevailed over imported materials, which is explained by the high costs for importing and transporting them. On the other hand, the absence of adequate equipment for the extraction and of personnel with experience in working with hard or very resistant materials, were also decisive for a more restricted use of the stone, mainly in masonry. In general, these materials were applied more frequently in administrative, civil, military and religious constructions. But they were also applied in the production of various elements in private constructions, built in towns and cities in the most important counties of Minas Gerais (Costa, 2009).

In the old Vila Rica, now Ouro Preto, there was always a great availability of quartzite rocks, which are present in the mountains around the city. One the types applied is known as Itacolomy quartzite and the other as Lajes quartzite. Itacolomy quartzite was the material with the greatest use in constructions of the 18th and 19th centuries, due to its geological characteristics. Unlike other quartzite in the region, this one is usually purer and does not have planar structures, which could lead to its partition depending of its use, as it may happen with the Lajes quartzites. Being more compact, it has little or no breakdown (sanding) in the extraction area, which qualified it to be worked manually with the use of a pick, for the production of cymbals, columns, corners, jambs or shutters. When compared to other non-local types, this quartzite has higher absorption capacities (Costa, 2009), which can compromise applications in places subjected to more frequent humidity.

It is known that quartzites have their properties defined by their degree of purity and by the conditions of metamorphism that generated them, always from sandstone transformations. In the case of quartzites in the Ouro Preto region belonging to the Itacolomy Group, as such as the eponymous quartzite, or the ones belonging to the Moeda Formation, as such as those in the Lajes region, the conditions of metamorphism were low, which means a low rate of recrystallization and compaction resulting in the permanence of a larger volume of spaces between grains, which may explain its absorption and porosity characteristics. These quartzites are not entirely monomeric. Therefore, the presence of other mica and opaque minerals interfere with their textural arrangements, and it can mean compromises in their applications. When normally altered, mica minerals can generate secondary minerals, as such as clays, which have expansive character and normally experience expansions where they are naturally located prior extraction. These secondary minerals can be further dissolved, creating voids that lead to sanding. When in oxidizing conditions, opaque minerals change and can cause extensive chromatic variation in these rocks.

When we compare Itacolomy quartzites with those that were and still are extracted in the Ouro Preto mountain range in the region known as das Lajes, it can be said that the latter, identified as Lajes quartzite, are more impure and characterized by the presence of high mica content, which contributes to the presence of planar structures or schistose in these rocks, which in turn allows them to be extracted according to these structures and resulting in the production of plaques. Because quartzites detach more easily, they were widely used in various coatings, including floors and sidewalks in Ouro Preto (COSTA, 2009). Another characteristic of these quartzites concerns their high content of opaque minerals (oxides and sulfides), which can cause extensive chromatic variations in these rocks under oxidation conditions. Shades of pink, red, yellow and orange, are much more common in the Lajes quartzites, when compared to the Itacolomy type.

In view of all these issues, it is possible to notice, especially in Ouro Preto, that the rocks used in its monuments can present quite significant variations ranging from granular to chromatic, often in the same building, especially when they involved the use Lajes quartzites. This situation also serves to verify that there was no criterion in the process of choosing these materials.

Specifically, in relation to the quartzite used in the *Chafariz da Glória*, it can be said that it was extracted in the Itacolomy mountain range. It is characterized by the presence essentially of quartz and low content of white micas (sericite) and opaque minerals, such as oxides and sulfides. From the set of opaque minerals, the presence of hematite to some ilmenite stands out, with also secondary production of limonite. Both in the monument (Figure 4) and in samples collected in the mountains (Figure 5), there is also the presence of tiny and rare fragments of very fine-grained black color material, which may represent fragments of rocks rich in clay. As for the color of these rocks, there is a predominance of whitish tones, and some other variation indicated by the presence of areas with grayish or silver colorations, and the presence of sericite more rarely yellowish and reddish. The latter can be explained in terms of changes in opaque mineral crystals, which are sometimes present, forming lines of opaque minerals. The presence of local areas with colorings ranging from greenish to black (crusts) is related to the presence of biological colonization.

Figure 4: Detail of texture, color and granulometry of Itacolomy quartzite at *Chafariz da Glória*. Source: authors' file, 2020.

Figure 5: Detail of the texture, color and granulometry of the Itacolomy quartzite from the sample collected in the old extraction area. Source: Source: authors' file, 2020.

4. CONSERVATION AND RESTORATION INTERVENTIONS IN THE 20TH AND 21TH CENTURIES

The *Chafariz da Glória* has been undergoing restoration and conservation works since the 19th century. However, only a few had the services performed registered. During the twentieth century, the first documented work was carried out in 1928, when there was the removal of the bamboo grove located behind the wall of the fountain, the deepening of the Latin inscription and the restoration of the damaged ornamentation in cement (Ministry of Education and Health, 1944). Between 1935 and 1937, other works were carried out as determined by the National Monuments Inspectorate, under the guidance of the engineer Epaminondas de Macedo (Figure 4). On that occasion, the three frowns were repositioned with the placement of the spouts, the front wall was cleaned and limewashed, the tank was restored, the railing that surrounded the fountain was removed and also services were done for reappearance of the water pipeline, which came from the top street. According to reports in the Annals of the National Historical Museum, repairs were around 1: 578 $ 075 kings, Brazilian currency of the time (Ministry of Education and Health, 1944).

In 1954, the fountain was included in the Construction Plan of the National Institute of Historical and Artistic Heritage (IPHAN), with general cleaning and repair services done on it. According to the Municipality of Ouro Preto (2011), between 1958 and 1959, among the restoration works undertaken by IPHAN, a study was carried out to manage the fountain, aiming at enhance its urban landscape insertion (PMOP, 2011). In 1975, the Engineering Department of IEPHA presented budgets and specifications referring to restoration services to be performed at the fountain. According to Rogério Diniz Gomes, who was in charge of the services, it would be necessary to carry out repairs and grouting of the stonework, repairs to the hydraulic piping, cleaning the stonework with the removal of native plants and painting with latex paint (PMOP, 2011).

In the 21st century (in 2011), the Municipality of Ouro Preto completed a full project for the restoration of twenty-two fountains located in the city, among them, *Chafariz da Glória.* According to the PMOP (2011), the *Chafariz da Glória* was considered to be in good condition, with soiling, moisture stains and hair cracks in the tank, the presence of biological agents, and the stone elements had specific pathologies caused by weathering such as: scaling in the panel, differential erosion and random discolorations. The blistering located at the vertices of the left column, which will be described later, were classified as granular disintegration.

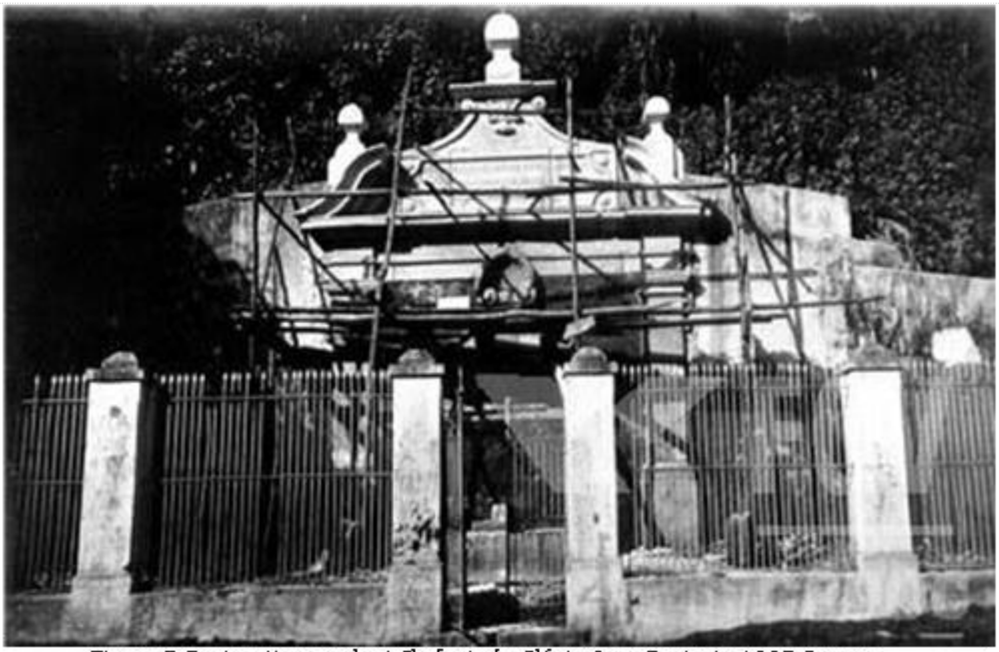


Figure 5: Restoration work at *Chafariz da Glória*, Ouro Preto, in 1935. Source: http://www.fgv.br/cpdoc/acervo/arquivopessoal/GC/audiovisual/aspectos-de-obras-de-restauracao-de -churches-and-monuments-made-by-the-service-of-the-historical-and-artistic-national-heritage. Accessed on February 6, 2021.

Regarding the services and materials used, as well as the diagnosis, the project treats all fountains in a generalized way, only differentiating some procedures according to the type of stone used. Regarding the consolidants, the project mentions some methods of application and, for a better choice, it indicates the need to carry out previous tests in the laboratory. However, they were not carried out in the execution of the work in 2015. The tests were carried out in loco, in small areas of the stone, directly over the monument. As consolidants for quartzite, the following were indicated: ethyl silicate; alkyl-alkoxysilane; mixture of ethyl silicate, alkyl-alkoxysilane and alkyl-aryl-polysiloxane. For the consolidation with mortar, the mineral base mixed with quartzite powder was indicated, without the presence of cement. To clean the stonework, it was recommended the use of laser, low pressure water, neutral soap (1:7, cyclohexyl methyl potassium oleate in water or detertec), specifying each product according to each type of damage. For biological patinas, herbicide was recommended, and depending on the situation, micro sandblasting. In the surface protection of the elements in quartzite rock, the following indications were made: mixture of acrylic resins, silicones and alkyl-arylpolysiloxane, to establish a protection against chromatic modifications, and to add the solution to be used with UV filtering products. Physical barriers were indicated as a solution for protection against humidity, as well as the construction of a ventilation ditch, with and without filling. In the case of situations considered more serious, where there was contamination by soluble salts, the barrier with polyester resin was indicated along the masonry (PMOP, 2011). However, the barriers were not implemented, as well as any intervention for drainage of the waters coming from the slope. The other services were made. However, they were not followed as indicated in the project.

As mentioned, the works of conservation and restoration of the Fountain were started and completed in 2015. Through verbal communication with the responsible restorer, Rinaldo Urzedo, information was obtained on the main procedures and substances applied in the fountain: for cleaning, water and a nylon brush were used in the stonework; for the desalination, plasters of distilled water were made and applied to the quartzite pieces. After this procedure, the biocide was applied by spraying it with 12% quaternary ammonium solution.

For the consolidation of the smaller grains, spraying with ethyl silicate was carried out, as the surface was more rigid, and it was not possible to quantify the amount of substance applied. The punctual pre-consolidation of rock slabs that were loosening was carried out with the application of acrylic resin mortar and stone powder, with the use of tweezers, avoiding the penetration of water in the scales, mainly in the frowns and in the entablature. Finally, Rinaldo affirmed that the lack of preventive conservation is the major problem of the fountains. He also pointed out that the desalination process should be carried out constantly, and if possible, with the use of cellulose pulp plasters instead of water.

After almost six years since the last intervention, some degradations noticed have worsened the conditions of the monument over time. The main one is the flaking and the appearance of blistering concentrated mainly on the vertices of the pillar on the left side of the fountain, more precisely in the shaft, with the presence of biological colonization. In the conservation and restoration project of *Chafariz da Glória*, carried out in 2011 by the Ouro Preto City Hall, the presence of this degradation was not mentioned.

5. CURRENT STATE OF THE MONUMENT

As already mentioned, the monument under study is a fountain of the parietal type in support of mortar stone masonry, which supports part of the slope covered by low growing vegetation of great size. In most part of the year the undergrowth is dense, due to the lack of maintenance. The land descends towards the left side of the fountain, accessing its rear part, which causes greater circulation and accumulation of water on that side. As a consequence, it was observed in loco that there is a greater concentration of damage on that same side (Figure 6). In addition, the non-existence of a drainage system, that could guide the waters coming from the slope and prevent the accumulation of moisture behind the wall, is evident by the presence of moisture throughout the length of the wall, either by the presence of stains caused by drained or concentrated water in the mortar region, or by the presence of other types of deterioration patterns, which has water as the main inducing agent. These other types are saline efflorescence and the proliferation of agents of biological origin.

The *Chafariz da Glória* currently has no damage that could compromise its structural stability. However, it presents superficial degradations that can be considered worrisome, with the presence of swelling, flaking and disintegration, mainly concentrated in the vertices of the niche on the left corner, more precisely in the shaft, and with the presence of microalgae between the flaking plate and the stone integrates (Figure 7).

Figure 6: Both pictures from the column on the left side of the fountain, with the highest concentration of degradations. Source: authors' file, 2021.

Figure 7: Detail of the greenhouse, where microalgae grow. Source: authors' file, 2021.

The flaking parts are very powdery and soft. Even if the diagnosis of the conservation status of the Fountain, elaborated in 2011 as a basis for the Restoration Project (PMOP, 2011), does not point to the mentioned degradation, it can be observed in photographic records of the time, which already indicated the presence of changes in the stone at these same points, as well as in older records (Figure 8-11). After the restoration in 2015, the pathologies seem to have been remedied (Figure 11). However, after a period, the degradation process was reactivated, worsening the monument's state of conservation (Figures 12 and 13).

Figure 8: Photographs of the Fountain in 1930 and 1940, respectively. The degradations on the left side of the monument are not yet visible. Source: Luiz Fontana Collection. Accessed July 1, 2020. https://ouropreto.mg.gov.br/luizfontana.

Figure 9: Photograph of the Fountain in 1946. Evidence of degradation appears on the left side. Source: Luiz Fontana Collection. Available at: https://ouropreto.mg.gov.br/luizfontana. Accessed on July 1, 2020.

Figure 10: Photograph of the Fountain in 2007. Source: Katia Maria Nunes Campos, 2007.

Figure 11: Photograph of the Fountain in 2011. Source: Estilo Nacional, 2011

Figure 12: Photograph of the Fountain right after the restoration. Source: National Historical and Artistic Heritage Institute, 2015.

Figure 13: Photograph of the Fountain with the degradations in the left column visible again. Source: Fernando Cardoso, 2018.

In the stone material used in the construction of *Chafariz da Glória*, there is physical disaggregation of the stone (Figure 14) mainly concentrated in the parts that make up the body of the fountain, such as basement, columns and frowns, and there is a detachment of isolated grains. Associated with this, there is another degradation pattern known as erosion (Figure 15), which promotes a loss of the original surface leading to the smoothing of contours or the modification of roughness (Vergès-Belmin et al., 2008). In the case of the fountain, there is also the performance of another erosive process identified as rounding, which causes, as the name says, the rounding of edges and vertices of the quartzite blocks, resulting in the loss of details and contours.

Figure 14: Quartzite swelling and breakdown. Source: authors' file, 2021.

Figure 15: Scaling and erosion, with rounding of vertices and edges. Source: authors' file, 2021.

In the places where these above-mentioned degradations occur, blisterings are formed (greenhouses) (Figure 16), that is, the detachment of a superficial layer of the stone originated by the formation of an elevation in a substantially hemispherical and hollow shape (Vergès-Belmin et al., 2008). The space generated by the greenhouse favors an environment conducive to the growth of microorganisms, with sufficient temperature, humidity and protection from the incidence of solar radiation. The presence of biological colonization, such as mosses and microalgae, can be noticed (Figure 17).

Figure 16: Blistering (stuffing). Source: authors' file, 2021.

Figure 17: Colonization by microalgae and mosses. Source: authors' file, 2021.

The damages of biological origin found in the fountain are mainly concentrated in the stone materials present in the columns, in the tank, in the central medallion and in the crowning of the monument, as well as in some areas of the retaining wall. Among them, colonization by plants, microalgae, cyanobacteria, fungi, mosses and lichens.

It is known that the pioneer colonizers of stone materials are autotrophic organisms, as such as lichens, cyanobacteria and microalgae. Lichens are associations between a green alga (or a cyanobacterium) with a fungus, belonging to the Fungi Kingdom, and they are grouped into three categories according to their morphology: the crustaceans that grow embedded in the substrate; the leafy ones that look like leaves; and the fruitful ones that have finger-like projections. Lichens form colonies of different colors and modify the environment in which they are installed by the production of organic material and excretion of organic acids that help the formation and thickening of the soil, enabling suitable conditions for the later and gradual installation of other living beings. They also exert a mechanical action on the substrate by penetrating the hyphae (Caneva et al. 2000; Prado et al, 2009; Tortora et al, 2017). At the Chafariz, they are mainly found at the crown, in the elements that are horizontal, as well as in the stony part of its central tank, and in apparently wetter places (Figure 18).

As already mentioned above, the microalgae are seen in the *Chafariz* as the greenish colonizations found under the places where there is flaking or swelling of the quartzite rock. They are also found where there is a higher concentration of moisture in the materials (Figure 18). Microorganisms, such as cyanobacteria and microalgae (Figure 19) form biofilms on the surface of the stone that are characterized by the heterogeneity of their community, by the interactions between its components, and by the production of different exopolysaccharides that protect them and allow them to adhere to the stone (Guiamet et al., 2008; Jayakumar; Saravanane, 2010; Madigan et al., 2016). These biofilms have varied thickness and colors, are strongly adhered to the substrate, and allow the deposition of organic residues that favor the growth of other organisms. In addition, they can cause dissolution of the rock (Tiano, 1998; Caneva et al., 2000; Prado et al., 2009).

Figure 18: Colonization of the stone by lichens. Source: authors' file, 2021

Figure 19: Colonization by microalgae. Source: authors' file, 2021

As already reported by Prado *et al.* (2009), in Ouro Preto, the vegetation, especially herbaceous and bryophyte species, is quite conspicuous and commonly found in fountains, retaining walls, bridges, staircases and church roofs. Among the damages caused by these vegetations, it can be mentioned the formation of holes caused by the penetration of moss rhizodes and the mechanical and chemical action (acid exudates) of the roots of vascular plants (Guiamet et al., 2008). Mosses, which are avascular plants, can be found in open cavities on the surface of the stone. At the Fountain, it is possible to observe them mainly at the joints of the stones (Figures 20 and 21). In addition, in some points of the fountain, as such as the crown, central tank and on the retaining wall, the presence of a layer of dark colored biofilm associated with the presence of mosses is noticeable. However, with the direct incidence of solar radiation, currently, this layer is dry and brittle, therefore, inactive.

Figure 20: Colonization of moss at the column joint: authors' file, 2021.

Figure 21: Colonization of moss in the joint between the stone parts of the tank: authors' file, 2021.

It is also possible to check the growth of ferns (*Pteris vittata L.*) and an invasive herbaceous plant, the species *Polygonum capitatum* Buch.-Ham (Figures 22 and 23). These plants can be seen in the fountain, mainly in the upper part, in the stones that have a flat and a horizontal surface. The presence of these plants in the Fountain is worrying, since their roots can develop in joints or in small fractures of the stones, causing their widening and, consequently, a rupture of the stone. In addition to this physical damage, the plants can cause chemical damage, besides retaining moisture, contributing to other degradation processes as such as saline efflorescence (Caneva et al., 2000; Prado et al., 2009).

Figure 22: Presence of fern (*Pteris vittata*). Source: authors' file, 2021.

Figure 23: Presence of the *Polygonum capitatum* Buch-Ham plant. Source: authors' file, 2021.

One of the main degradations observed in the fountain is closely related to the composition of the Itacolomy quartzite and is has to do with chromatic variations that can be explained by the alteration of opaque minerals, as such as oxides and sulfides and micas, which can be part of the rock. In the absence of these materials, this quartzite tends to be whitish (Costa, 2009). In the fountain under study, the presence of these chromatic variations noted had already been installed even before the extraction of the material, but they were partially intensified by the action of biological agents. The local presence of areas with colors ranging from greenish to black (crusts) confirm these interferences due to the presence of biological colonizations.

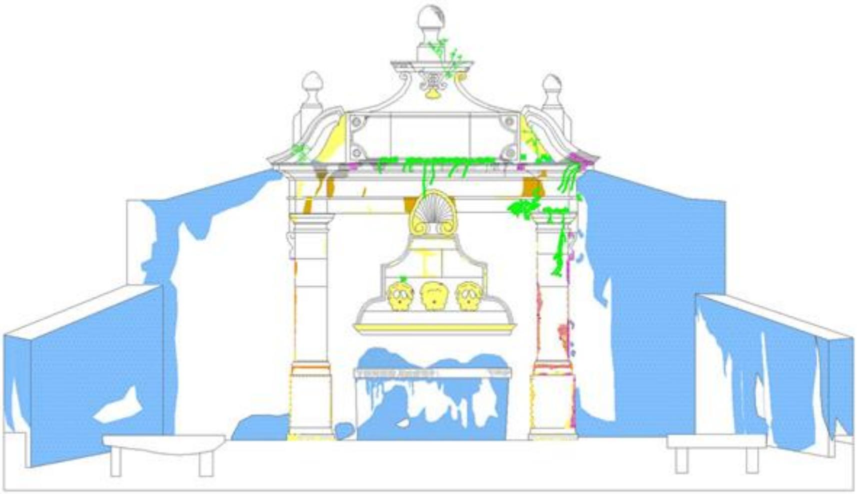
Regarding the part of the fountain in masonry made of mortar stone, it is possible to notice spots of dirt, loss of the pictorial layer and fungal colonization. Fungi, part of the Fungi Kingdom, are multicellular except for yeasts, are chemoheterotrophic and acquire nutrients by absorption (Tortora et al., 2017). In general, the following deterioration actions caused by fungi can be highlighted: aesthetic damage by the formation of dark pigmentation biofilm, due to the release of pigments or the very presence of hyphae (Figures 24 and 25); metabolic production of acids with consequent solubilization of the stone, and penetration of the mycelium in the structure of the materials, increasing its porosity and enabling greater water retention (Gómez-Alarcón et al., 1995; Caneva et al., 2000; Videla, 2003; Ferrari et al., 2015).

Figure 24: Fungal colonization. Source: authors' file, 2021.

Figure 25: Generalized fungal colonization. Source: authors' file, 2021.

6. MAPPING DETERIORATIONS

Following the identification of the deterioration patterns observed in the *Chafariz da Glória*, they were mapped in an attempt to establish the relationships between their various causes and the agents of the degradations, with the characteristics and properties of the Itacolomy stone present in the Monument. In the elaborated map (Figure 26) it is possible to notice that a large part of the degradations is concentrated on the left side of the Fountain.



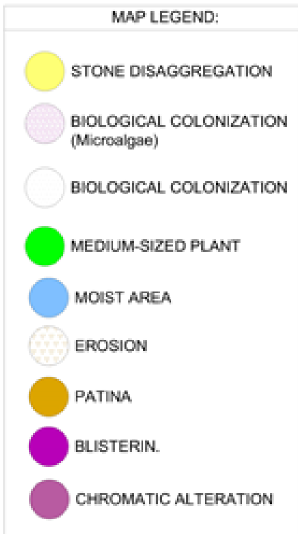


Figure 26: Deterioration Map of the *Chafariz da Glória* Source: authors' file, 2021.

From the mapping, some relationships were established between the degradations, their respective agents, probable causes and the characteristics of the materials, components of the fountain, in which this damage was observed (Table 1)

Table 1: Relationship among damages, their probable causes, and composition of the materials used to make the *Chafariz da Gloria*, in which the damages was observed. Source: authors' files, 2021.

DETERIORATION	AGENT	PROBABLE CAUSE	MATERIAL
PATINA	- Climatic variations. - Relative humidity. - Wind action.	- Exposure to bad weather. - Lack of preventive conservation.	Quartzite Stone.
MEDIUM-SIZED PLANT: (Pteris Vittata, Polygonum Capitatum Buch – Ham).	- Climatic variations. - Relative humidity. - Wind action. - Presence of organic matter	- Exposure to bad weather. - Water accumulation and favorable conditions for its development. - The surroundings with the presence of small to large vegetation. - Lack of preventive conservation.	Quartzite Stone.
BIOLOGICAL COLONIZATION	- Climatic variations. - Relative humidity. - Volume of precipitations and their chemical compositions.	- Exposure to bad weather. - Conditions favorable to their proliferation, especially the high humidity. - Presence of organic matter and microorganisms.	Quartzite Stone.
BIOLOGICAL COLONIZATION - Microalgae. - Mosses. - Lichens. - Fungi.	-Presence of organic matter. - Presence of oxygen. - Climatic variations. - Relative humidity.	-Exposure to bad weather. -Favorable conditions for their proliferation.	Quartzite Stone. Lime-based pictorial layer.
MOIST AREA	- Forces resulting from the kinetic energy of raindrops. - Capillary rise forces. - Forces of gravity. - Wind pressure forces - Environmental factors: climate, solar radiation, temperature and rainwater.	- Rain action. - Ascension moisture coming from the soil. - Absorption and penetration of rainwater. - Condensation humidity. - Moisture due to the hygroscopicity of the materials. - Wet soil conditions. - Use of porous materials, with capillary vessels capable of carrying water.	-Quartzite stone. -Mastered stone. - Coated with sand and lime.
EROSION	- Physical factors 0 Weather	- Accumulation of water, wind action (bad weather)	- Quartzite Stone.
CHROMATIC ALTERATION	- Natural Stone Composition; - Moisture;	Oxidation of opaque mineral contents (oxides and sulfides) of the stone	- Quartzite Stone.
CHROMATIC ALTERATION	- Metallic oxidation reaction residue	- Oxidation of water conductors	- Quartzite Stone. - Copper conductor.
STONE DISAGGREGATION	- Chemical factors - Biochemical factors	- Constant exposure to moisture and salts - Crystallization of salts by evaporation of water; - Specific and natural characteristics of the stone; - High stone absorption capacity; - Chemical interaction between microorganisms and stone	- Quartzite Stone.

BLISTERIN	Chemical and Physical Factors	-Constant exposure to moisture and salts - Crystallization of salts by evaporation of water; - Specific and natural characteristics of the stone; - High stone absorption capacity;	- Quartzite Stone.

7. RESULTS AND DISCUSSIONS

The *Chafariz da Glória* built in 1752 and listed as a national artistic heritage in 1950 is one of the most important urban monuments in the city of Ouro Preto, MG. Currently disabled, it now serves as a documentary, historical and cultural record in the landscape of the complex urban city. In view of its relevance, all possible efforts must be taken for its preservation and conservation.

This work is putting into evidence the first investigations regarding the causes and agents that have motivated the degradations suffered by the stone material used in the monument, the Itacolomy quartzite. A mapping of the damage was developed based on a detailed survey of the *Chafariz* history, including the various conservation and restoration interventions suffered over the years (in the 20th and 21st centuries), the identification and description of current degradations, and the macroscopic characterization of the stone. The map made possible to relate, preliminarily, the degradations to their motivating agents and causes, and these with the characteristics and properties of the stone and the interventions that the fountain had undergone until today.

Basically, the degradations observed in the *Chafariz* and the presence of agents of biological origin are associated with the presence of humidity, which is evident in several areas of the Monument. On the other hand, the characteristics of the Itacolomy quartzite stone used in the Monument, as such as the higher absorption capacity and porosity, which were verified in the sample obtained in the extraction area, and due to the low rate of recrystallization and compaction, also make the stone more susceptible to degradation when exposed to a constant humid environment (Costa, 2009). The presence of clays and of clayey material in the stone, indicated by the occurrence of black colored fragments, also contributed to the deterioration patterns. In the presence of moisture, these clays have expanded, generating voids provoking sanding. Finally, chromatic variations, a function of humidity and oxidizing conditions, complete the set of degradations present.

The colonization of lichens, fungi, mosses, microalgae and plants, the main agents of biological degradation observed, are notorious in the *Chafariz*. These colonizations are present in points and areas where moisture is present. In addition, the conditions of the ongoing degradation have allowed these biological agents to act, which in turn can further contribute to the deterioration of the degradations in the stone.

In conclusion, the behavior of the biological agents has significantly contributed to the worsening of the stone degradations. They interact with the bedrock and modify it, which explains the alterations of color and the disaggregation of the stone.

In view of the investigations carried out so far, it has not yet been possible to establish contributions or accurate relationships between the conservation procedures and the substances applied in the last restoration intervention done in 2015 with the deterioration of the Monument's state of conservation.

Since this study has the future goal of proposing consolidation solutions for the *Chafariz da Glória*, meaning more long-lasting conservation, in the next phase of the research it will be necessary to seek answers for some of the damages already observed. If humidity presents itself as the main agent that has triggered the degradation processes, it is essential to know its origin in detail. Moreover, it will be necessary to detail the areas in which humidity plays a more relevant role. To search for its presence and, identify it in case it is found.

There is also evidence that the presence of salts has corroborated the degradation processes. Thus, it is necessary to confirm this assumption even with the identification of the salts that have acted in the Monument.

Finally, there is no doubt about the performance of the processes of disaggregation of the Itacolmy quartzite, especially in the column on the left side of the *Chafariz da Glória*, motivated by the agents mentioned. However, for the position of consolidation actions, it is essential to know how deep this process has reached in the constructive element.

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Silica nanoparticles for stone consolidation: the role of the dispersion media on the treatment performances

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SUMMARY: Since recent years, inorganic nanoparticles have been explored for a use in alternative to traditional consolidants. Here we report on an experimental activity dealing with nanoSiO_2 in an alcohol dispersion (ethanol) applied to a highly porous limestone. Penetration depth was studied through SEM-EDS analysis and consolidation effectiveness was assessed by a low destructive penetration test and UPV propagation. Surface colour changes were measured and variations of the stone microstructure were investigated by Mercury Intrusion Porosimetry and a BET analysis. Effects of the treatment on the stone behaviour with water were evaluated through wettability measurements, water capillary absorption and vapour permeability tests. Results of the analyses and tests were coherent with a very low penetration of the nanosilica particles within the stone, which accounts for an almost absent consolidating effectiveness. These results, compared with those previously obtained from the same nanoparticles in water, show that the interaction of the nanosilica based product with the substrate and the consequent performances, strictly depend on the dispersion media.

KEY-WORDS: Nanosilica, Porous limestone, Penetration depth, Consolidation effectiveness

1. INTRODUCTION

Consolidation is a main issue in stone conservation when deterioration results in strong dechoesion phenomena. Among traditional consolidants, including both organic and inorganic materials, ethyl silicate-based products, mainly composed by alkoxysilanes, have been the most widely used. Alkoxysilanes polymerise in situ inside the pore, through a classic sol–gel process. They penetrate deeply into porous stone and show a good weathering-resistance, while important drawbacks are the poor chemical bonding to calcite, and the tendency to crack during shrinkage and drying [Wheeler, 2005].
Developing new products to obtain improved consolidating performances and long-lasting effects is a topic of great interest in stone conservation. In recent years, nanoparticles have received a lot of attention in order to minimize the drawbacks and negative effects of the traditional inorganic consolidants, i.e. the formation of microcracks in case of ethyl silicate based products [Miliani et al., 2007].
Moreover, several advantages rely on nanoconsolidants, such as nanosilica and nanolimes. In particular, nanosilica dispersions require a shorter curing time compared to ethyl silicate based consolidants, as gelation of silica nanoparticles takes place in only few days, while hydrolysis of ethyl silicate and subsequent condensation need several months [G.S. Wheeler, 2005; Scherer & Wheeler, 2009). In addition, they can be applied also on moist substrates and in very humid environment, although higher consolidating effectiveness has been obtained in dry environment [Zornoza-Indart & Lopez-Arce, 2016]. The effectiveness and the compatibility of nanosilica dispersions have been investigated on different substrates, such as porous limestone [Zornoza-Indart et al., 2016; Ruffolo et al., 2017], tuff [La Russa et al., 2014; Iucolano et al., 2019] and granite [Pozo et al, 2019]. One main issue has been found in the limited ability to penetrate deeply into the substrate, resulting in the accumulation of nanoparticles on the surface or close to it [P. Maravelaki-Kalaitzaki et al., 2008; Licchelli et al., 2014]. Nonetheless, penetration depths from about 6 mm up to 30 mm have been reached in the case of highly porous stones [Zornoza-Indart & Lopez-Arce, 2016; Vasanelli et al., 2019].
The penetration depth of stone consolidants within the substrates is critical for achieving a successful consolidation and it depends on the microstructural characteristics of the stone, as well as on the intrinsic properties of the consolidant like viscosity and surface tension of the liquid [G.S. Wheeler, 2005].

Among the various parameters having effects on treatment performance, the solvent used as dispersion medium may play a significant role [Sassoni et al., 2018; Petronella et al., 2018]. As an example, in the case of nanolime, the use of alcohol allows carrying higher amount of lime nanoparticles, yields deeper penetration with less water and induces a faster carbonation [Otero et al., 2017].
In this paper, nanoSiO_2 in an alcohol dispersion (ethanol) was applied to a porous limestone. The study aims to assess the treatment issues compared with those previously obtained from the same nanoparticles in water, in order to achieve knowledge on the role of the solvents in the transport mechanism of silica nanoparticles within porous materials.

2. EXPERIMENTAL PROCEDURE

Materials and application of the consolidant product

The product used for the stone consolidation consists of nanosized SiO_2 dispersed in a water/alcoholic solution (17% w/w). It has a density of around 1.0 g/ml, a viscosity of 10 mPa/sec at 20°C and a pH of 8.0. The synthesis procedure is based on a sol-gel process starting from a sodium silicate solution in the presence of mineral acid (e.g., HCl) or a base (e.g., NH_3) as catalyst, which cause the precipitation of the silica.

The properties of precipitated silica depend strongly on the conditions of its synthesis, such as the synthesis temperature, time of precipitation, pH, the addition of surfactants, and approaches on washing and drying. The white powder is recovered by filtration followed by cleaning with distilled water in order to neutralize the acid or the base used and dried at a temperature of 60-80°C for about 12 h andre-dispersed in water to a pH value around 8.0. A stable nanodispersion of rounded silica particles is obtained, with NPs having a mean size of approximately 35 nm (PdI 0.20). This suspension was finally mixed with ethanol to obtain the final product.

The treatment was applied on a soft, very fine and whitish limestone, named “Pietra Gentile” or “Carovigno stone” [Calia et al., 2014]. Petrographically, this is a medium-fine wackestone [Dunham, 1962] made of fine bioclastic remains and lythoclasts, having sizes from some tens of microns up to 200 microns. They are contained in a micritic groundmass, finely mixed with small amounts of microcrystalline calcitic cement. A fine porosity of both interparticle and vug types is widespread throughout the groundmass.

Before the treatment application, the stone specimens were washed with deionized water and dried at 60°C until a constant weight was reached (two consecutive weight measurements was less than 0.1%). Then they were stored for 24h in laboratory conditions (22°C ± 2 with 45% ± 5% relative humidity) before the application of the nanosilica product. Treated specimens were leaved in laboratory conditions for one month before testing.

In order to compare the performances of the nanoSiO_2 dispersed in alcohol with those obtained in a previous research with the same NPs dispersed in water [Vasanelli et al., 2019], we applied the same quantity of solution, that is 100 mg/cm^2, corresponding to an amount of nanosilica of 30 mg/cm^2. We also adopted the same procedure of application, namely consecutive applications by brush, previously selected.

Test methods

The performances of the nanoconsolidant were investigated by several analyses and tests performed on the untreated stone and on the treated one, after one month from the application of the product.

Penetration depth and consolidation effectiveness

ESEM-EDS analyses. Environmental Scanning Electron Microscopy (Mod. XL30, FEI Company) combined with Energy-Dispersive X-ray Spectroscopy was used to investigate the penetration depth of nanosilica into the stone. A qualitative/quantitative elemental analysis was performed on sample cross sections using Si as an indicator of the nanosilica presence. Qualitative distribution maps of Si were obtained on sample areas of approximately 400x300 µm. Quantitative distribution profiles of Si were evaluated along line scans starting from the surface up to 20 mm of depth The obtained EDS spectra were normalized to the Ca peaks. The following analytical conditions were adopted: low vacuum mode, pressure of 0.7 Torr, beam accelerating voltage of 25kV, 100 Lsec acquisition time, 100 x 100µm area of each analysis.

Penetrometric test. The surface hardness of the treated and untreated stone was measured by a moderately destructive penetration test. An RSM (Response Surface Methodology) penetrometer (RSM_15 by DRC srl) was used. This instrument was designed to estimate the resistance of mortar joints to the penetration of a steel needle driven by strikes generated at a constant energy of 4.55 Nm. The penetration depth (expressed in millimetres) gives a measure of the surface hardness, as the higher the tip penetration, the lower the hardness of the surface. A stone ashlar of 53x8x10 cm size was used for the test. This was performed on the two faces of 38x8 cm size, one of which was treated. Five measuring points were considered for each treated and untreated face. At each point of measurement, the penetration depth of the tip was recorded at five steps, namely after 1, 2, 5, 10 and 15 strikes. The mean value at each fixed number of strikes was calculated.

Ultrasonic Pulse Velocity test. UPV measurements were carried out on the same specimens before and after the treatment to verify changes in the velocity propagation due to the application of the treatment. UPVs were measured according to the standard [ASTM D2845 – 08, 2008] by a direct transmission method. An Epoch 4 plus (Olympus) instrument and probes with a frequency of 1 MHz were used. A good contact between the transducers and the stone was ensured by a coupling gel. UPV measurements were repeated three times in each measuring point and the mean value was calculated.

Compatibility with the stone support

Compatibility of the treatment with the original stone properties, such as colour, microstructure and behaviour with water, was assessed. The following analyses and tests were performed on untreated stone samples measuring 5x5x2 cm and 5x5x1 cm; then they were repeated after the treatment was applied on one of the two largest sample faces.

Colour measurements. Changes of stone colour due to the application of the treatment were evaluated by colorimetry. Measurements by light absorption in diffuse reflection were performed by means of a Konica Minolta CM700d spectrophotometer [UNI EN 15886:2010]. A D65 illuminant under a 10° standard observer was used. Before the measurements, the device was calibrated with a white ceramic disk and a black trap portion. Measurements were performed on the surface of three samples, each one measuring 5x5 cm. They were taken in ten points for each sample. For each point three measurements were repeated and the mean value was automatically calculated by the instrument. The colour parameters L*a*b*were determined in the CIELab 1976 colour space. The colour variation (ΔE*) was calculated as:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where L* is the lightness/darkness coordinate, a* and b* the red/green and yellow/blue coordinates, respectively.

Porosity and porosimetric analyses. The influence of the treatment on the stone microstructure was evaluated by Mercury Intrusion Porosimetry (MIP) analysis in the range of 0.001-100 µm, using Pascal 140 Series and Pascal 240 Series porosimeters (Thermo Finningan). A BET analysis was also performed by means of a Gemini VII instrument (Micromeritics). Both these analyses were performed on three specimens of each treated and untreated stone. The stone after the treatment was investigated over a sample thickness of 5 mm from the treated surface.

Static contact angle measurements [UNI EN 15802:2010]. They were performed by means of a Costech apparatus. Ten measurements were performed on a sample surface of 5x5 cm.

- *Water capillary absorption test* [UNI 15801:2010]. Five specimens measuring 5x5x2 cm were tested. Progressive weight increases of the samples were measured and the amount of absorbed water (Q) was calculated as:

$$Q=(w_i - w_0)/A \quad (2)$$

where: w_i and w_0 are the weight of the sample at time t_i and t_0, respectively, and A is the area of the sample exposed to the water.

Water vapour permeability test [Normal-21/85]. Water vapour permeability was measured on five specimens measuring 5x5x1 cm. The water vapour permeability is defined as the mass of water vapour transmitted through a sample per area unit in a time unit, under defined conditions, and describes the ability of a material to allow water vapour passing through. The following equation was used to calculate the water vapour permeability:

$$WVP=\Delta M/(t^*A) \quad (3)$$

where ΔM is the weight change in the steady state (expressed in g), A is the area exposed to water vapour (in m^2) and t is the unit time (24 h). In all the cases, the used ΔM was the average of three consequent values of the daily difference in weight.

3. RESULTS AND DISCUSSION

Penetration depth and consolidation effectiveness

The investigated Carovigno stone is a pure limestone, almost exclusively made of calcite [Calia et al., 2014], thus Si is an effective marker for the evaluation of the amounts of the product at different depths within the treated stone. The EDS map of Si distribution shows the accumulation of nanosilica close to the stone surface (Figure 1). Distribution profiles of this element detected a penetration depth of the consolidant within the stone mostly up to 50 μm from the surface (Figure 2, a) and only in some points it reached 110 μm, approximately (Figure 2, b). It is worthy to note that the nanosilica accumulation takes place starting from about 20 μm under the stone surface.

These results strongly differ from those previously obtained with the use of nanosilica in water dispersion [Vasanelli et al., 2019]. A notably higher penetration depth, up to 8 mm was found in tahat case, and the distribution of the consolidant gradually decreased from the surface within the stone. In spite of the low penetration depth of nanoparticles dispersed in the alcohol, a notably higher depth of the wet fringe, close to 2 cm, was observed. This means that the wet fringe cannot be assumed as indicative of the presence of the product after drying. It may indicate the presence of the solvent, but not necessarily of the dispersed particles, as a phase separation between NPs and the solvent may have been occurred. Another possible explanation is that back-migration of nanoparticles with the solvent towards the surface may have taken place during dryng, with consequent accumulation beneath the surface. [Borsoi et al., 2016] report that nanolime dispersion in ethanol easily penetrates in depth in the stone substrate, with any accumulation during the absorption phase. Accumulation beneath the surface was found to occur during the solvent evaporation.

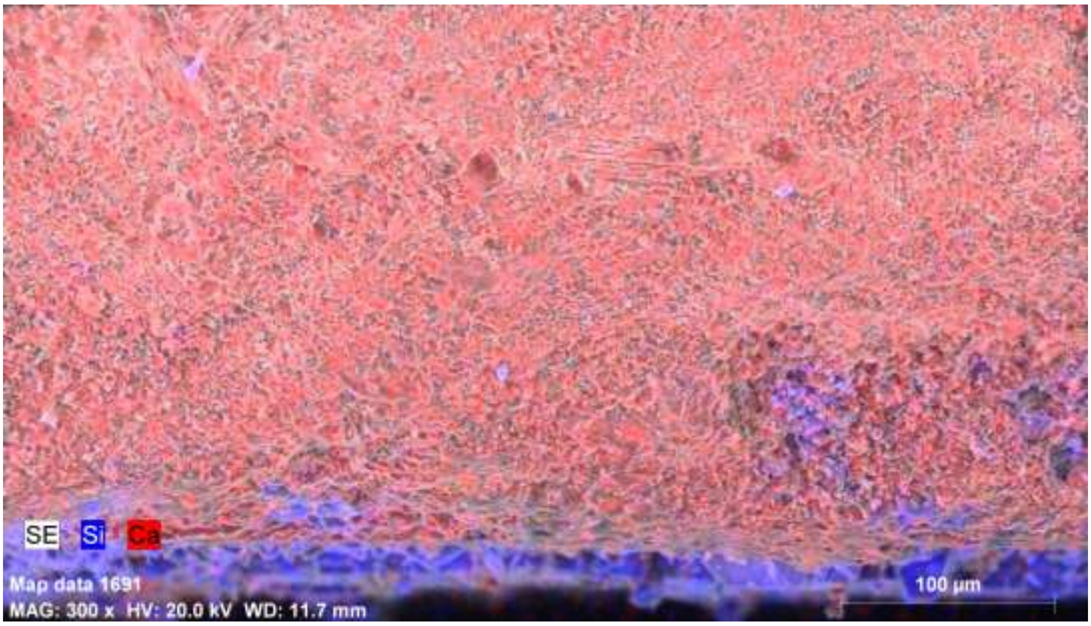

Figure 1 EDS distribution map of Si showing an accumulation close to the stone surface.

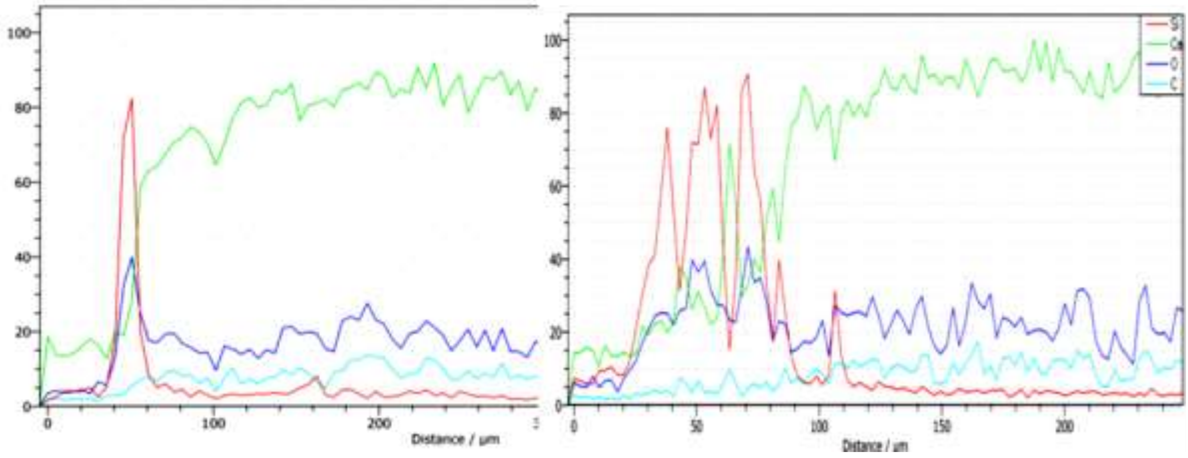

Figure 2 EDS profile of chemical elements detected within the stone concentration (% wt) with the distance from the surface, showing the accumulation of Si between 20 and 60 µm of depth (a); in some points Si is present up to nearly 120 µm of depth, although concentrated mostly between 20 and 80 µm from the surface (b).

The poor penetration of the product into the stone accounts for the increase of the stone hardness detected in the treated stone only close to the surface, as results of the penetration test for treated and untreated stone surfaces show in Figure 3. The penetration depth of the tip (ΔL) was registered at each step, namely under 1, 2, 5, 10 and 15 strikes and the standard deviation was calculated. The mean values of ΔL show that the tip penetration at the first step, that is under one strike, was lower in the treated stone compared to the untreated one. This difference could be attributed to the presence of the nanosilica layer close to the surface and related hardening effect. The advancement of the tip within the stone was nearly the same in treated and untreated samples at 2 and 5 strikes. The different responses obtained at the further steps of the test are likely the result of an intrinsic stone heterogeneity, as any hardening effect of the consolidating product may be supposed.

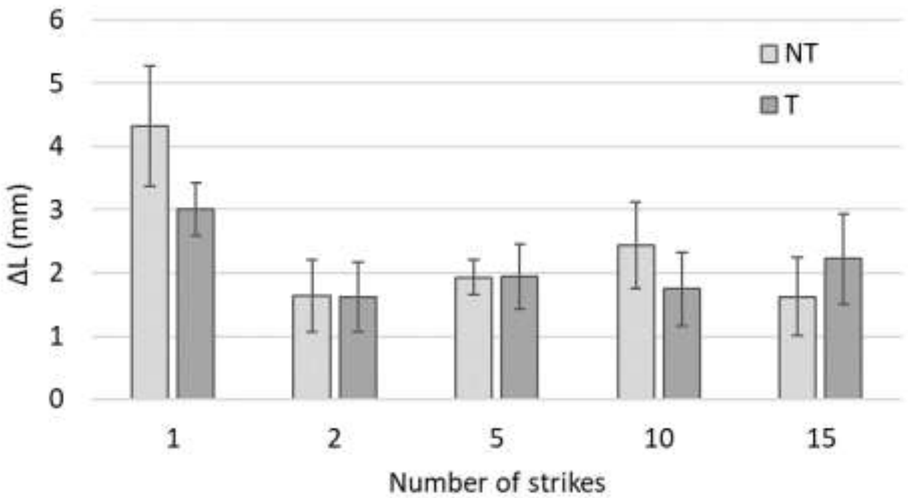

Figure 3 Penetration of the tip (ΔL) within treated (T) and not treated (NT) stone at each number of strikes.

No changes in UPVs were recorded in the treated stone samples after the consolidant application (Figure 4). Ultrasonic pulse velocity test is able to detect consolidation effectiveness through higher velocities of propagation in the stone after the application of nanosilica based treatments [Zornoza-Indart & Lopez-Arce, 2016]. In fact, the ultrasonic velocity propagation within the stone materials depends on a variety of factors relating to both composition and physical-mechanical characteristics [Török & Vásárhelyi, 2010; Vasanelli et al., 2015]. These characteristics may be modified by the application of a consolidating product

and the consequent wave velocity variations may be used as an index of the presence and/or the effectiveness of the consolidation [López-Arce et al., 2010; Sassoni et al., 2020].
Unchanged velocities recorded after the treatment are likely the result of a negligible incidence of the treated stone layers on the wave propagation, due to the poor penetration of the product into the stone.

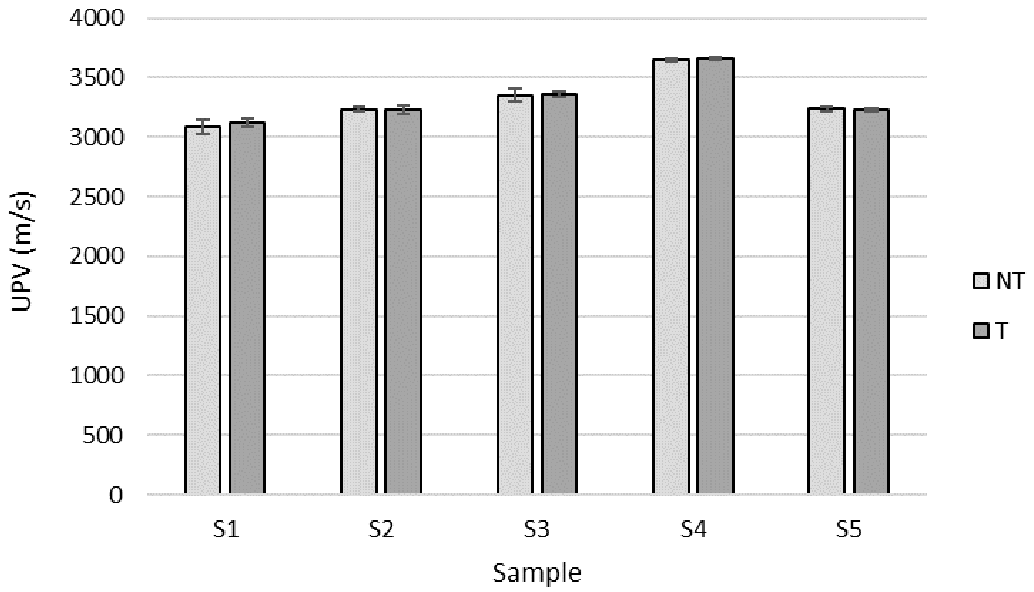

Figure 4 UPVs recorded in each specimen (S1-S5) before (NT) and after (T) the application of the nanosilica consolidant.

Changes of the physical properties

One of the basic requirement of a consolidant product is the compatibility with the stone substrate, namely the attitude of not altering significantly the aesthetical, physical and microstructural properties of the original stone [Delgado Rodrigues & Grossi, 2007].

As regard the influence of nanosilica on the aesthetical aspect of the stone, results of colorimetric measurements (Table 1) show negligible variations for L*, a* and b* coordinate on the stone sample surface after the treatment. The values of the overall colour changes (ΔE*) remained always under 1, that is notably below the threshold value of colour changes visible to naked eyes.

Accumulation of silica nanoparticles on the surface of Carovigno stone has been found to produce significant color variations [Calia et a.l, 2012]. The low modifications of the colour properties detected in this case are probably due to the fact that accumulation of silica nanoparticles does not take place on the stone surface, but at about 20 micrometres within the stone.

Table 1 Colorimetric test results on stone specimens before and after nanosilica application.

Specimen		Before treatment			After treatment			
		L*	a*	b*	L*	a*	b*	ΔE*
C1	Mean	93,73	0,53	5,37	93,21	0,52	5,62	0,58
	St. dev.	0,77	0,08	0,51	0,80	0,04	0,42	
C2	Mean	89,81	1,52	6,96	89,05	1,61	7,55	0,96
	St. dev.	1,16	0,62	1,18	1,19	0,79	1,53	
C3	Mean	90,89	0,87	6,12	90,14	0,90	6,55	0,86
	St. dev.	0,87	0,10	0,48	0,93	0,09	0,42	

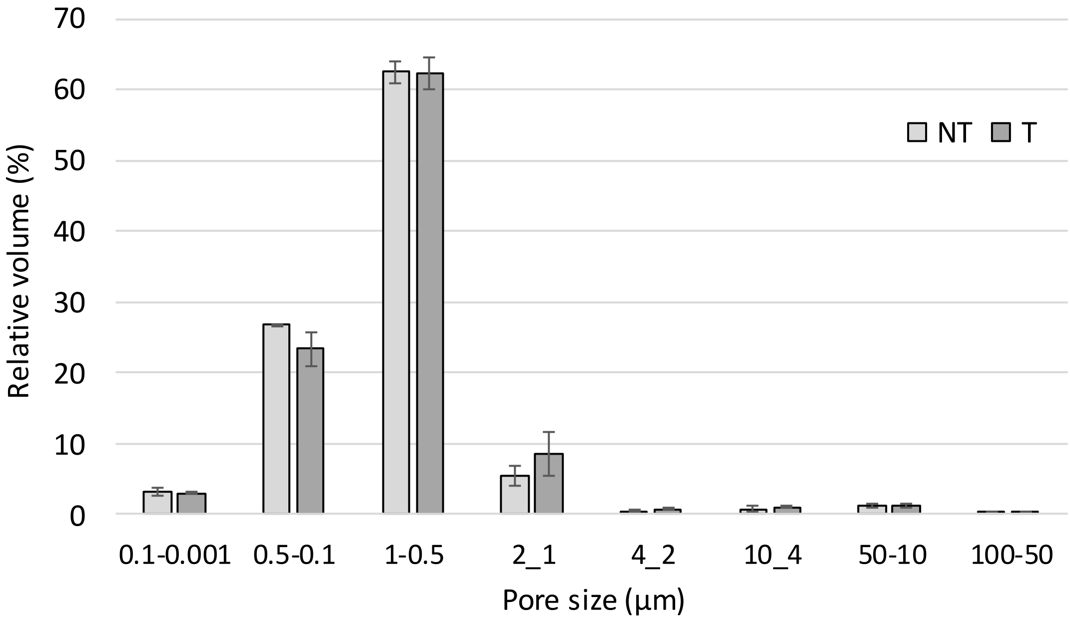

Figure 5 MIP results of treated (T) and not treated (NT) specimens.

MIP analyses, aiming at evaluating the effect of the nanosilica filler on the stone microstructure, showed slight changes of the integral open porosity after the treatment, passing from 18.11±0.72 to 19.76±1.14. Nor the accumulation of nanosilica particles in a few tens of micrometres was found to significantly alter the porosimetric distribution in the investigated pore size range (Figure 5). In the treated specimens, only a slight reduction of the presence of pores with radii between 0.5 and 1 µm and a slight increase of those with radii in the range between 2 and 1 µm was recorded. Indeed, the stone was investigated over a sample thickness of 5 mm from the treated surface, notably higher than the thickness of the stone involved in the treatment, so that the detected modifications are likely underestimated.

Brunauer, Emmet e Teller (BET) analysis was performed to investigate if nanoparticle fillers affected the pore system out of the lowest pore dimensions investigated by MIP. Results showed an isotherm typical of a macroporous solid (type III) associated to the stone before the treatment (Figure 6). It changed to an isotherm typical of a mesoporous solid (type IV) in the treated stone. A corresponding increase of the measured surface area was found, from 0.44 m^2/g (c parameter equal to 47.1) to 2.51 m^2/g (c parameter equal to 91.8). Applying the Barret, Joyner e Halenda (BJH) model, after the treatment the cumulative volume of pores in the range between 17and 3000 Å was 0.0052 cm^3/g, which corresponds to a relative volume of 1.35 % (considering a stone density of 2.7g/cm3).

Microstructural changes showed by the modification of the isotherms and increase of the pore surface area are consistent with reduction of pore spaces due to partial occlusion and with the high specific surface area of the nanoparticles within the stone porous structure. Nonetheless, they could be also attributed to the dectection of a microporosity probably inherent to the nanoparticles accumulation layer close to the surface,

The behavior against water is a further critical issue with the consolidation treatments, as the products introduced within the stone structure can modify the circulation of water with implication on the stone durability. The application of the nanosilica dispersion strongly changed the wettability of the stone surface, which is very sensitive to many factors influencing contact angles between the water droplets and the substrates [Della Volpe et al., 2000]

The contact angle measurements failed on the untreated stone, as water absorption was very high and rapid, and no drop formed on its surface. On the contrary, the contact angle measured on the specimen surface after the treatment was 31.42°±3.60°.

The presence of the consolidant was found to influence the water capillary absorption in the early stage of the test (Figure 7). The kinetics of the water uptake reduced, especially in some samples (T_3, T 4 and T 5). The amount of water absorbed at the end of the test remained almost unchanged or slightly reduced. The maximum percent of reduction was 6% in one of the samples (T_3). Therefore, it seems that nanosilica accumulation in the outer stone layer close to the surface does not act as a barrier to the water penetration. Rather it slows down the initial absorption rate, while it slightly affects the total water uptake.

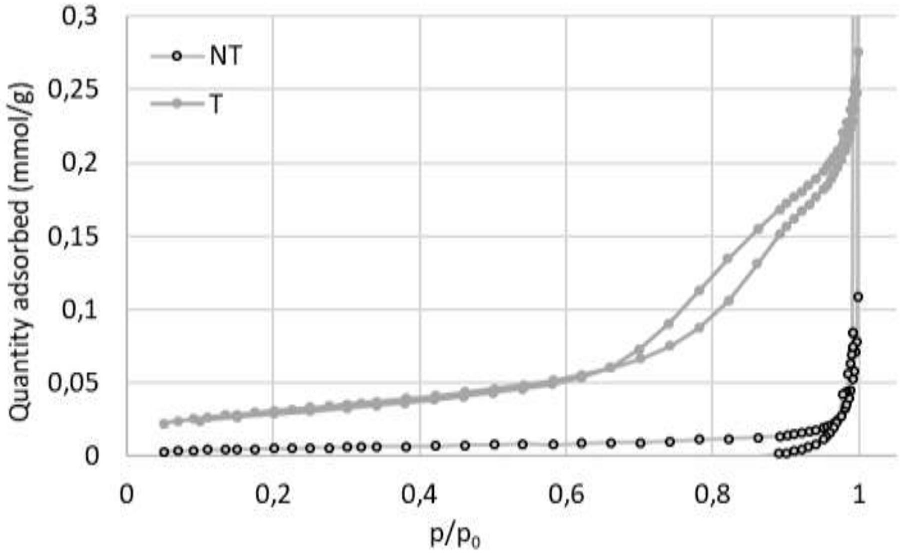

Figure 6 Isotherm curves obtained from BET analysis for treated (T) and not treated (NT) stone specimens.

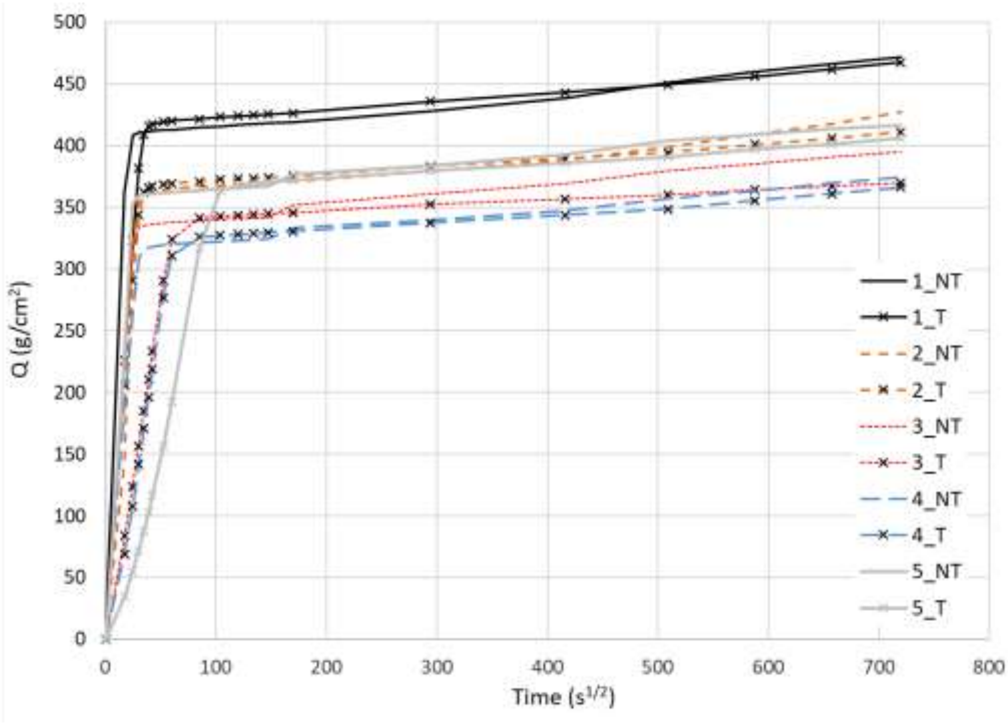

Figure 7 Water absorbed by capillarity (Q) versus the square root of time for each tested specimen before (NT) and after (T) the treatment.

The mean value of water vapour permeability was 160.35±53.91 g/(m224h) before treatment and equal to 172.50± 70.40 after treatment. The behaviour under the test was not the same for the investigated specimens (Figure 8). A slight decrease of the permeability, equal to 5%, was measured for the P2 specimen. The nanosilica treatment caused an increase in WVP values for P1 and P3 specimens, equal to 13% and 10%, respectively. Water vapour permeability increase has not an immediate explanation. It seems that rather than pore occlusion, other factors take part in the vapour transfer across the samples. Higher permeability has been found in marble samples [Kronlund et al., 2015] and in membranes [Dumée et al., 2011] functionalized with fluorine-based hydrophobic thin coatings, as related to a probable lower condensation phenomenon on the hydrophobic pore walls. Consequently, the diffusion rate of water vapour through hydrophobic pores was higher than the diffusion rate through hydrophilic pores. This effect was found neutralized when the polymer layer onto the pore walls was thick enough to reduce the pores' dimensions.

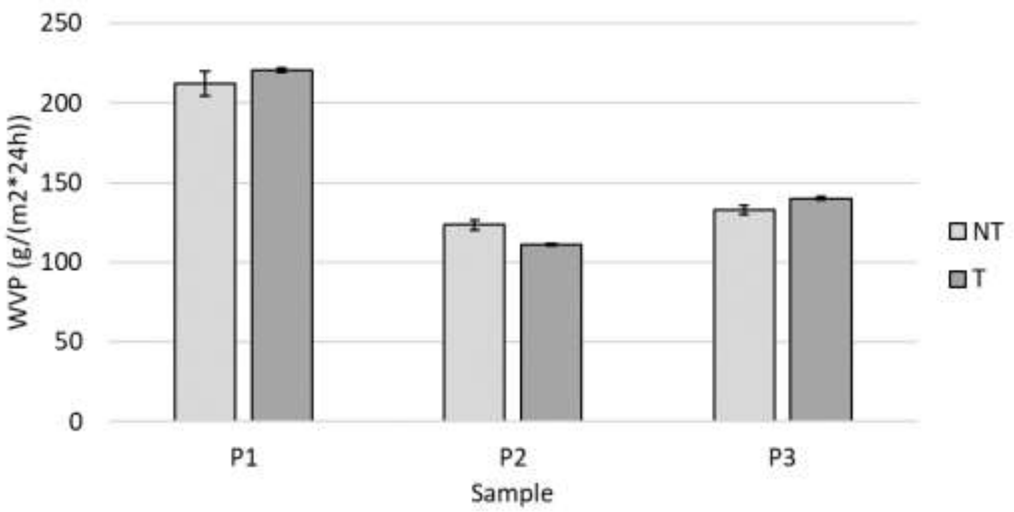

Figure 8 Water vapour permeability of treated (T) and not treated (NT) specimens

4. CONCLUSIONS

Consolidation of natural stone, as a material of interest in the field of Cultural Heritage, is one of the main issues with conservation and developing new products to obtain improved consolidating performances and long-lasting effects is a topic of great interest.

In this paper a nanoconsolidant consisting of silica nanoparticles in ethanol dispersion was applied on a porous calcareous stone. The study aims to investigate the treatment performance in relation to the alcohol solvent.

The overall results show that the use of nano-SiO_2 dispersed in alcohol lead to a very poor penetration of the nanoparticles within the stone, producing an accumulation layer just under the surface, with a maximum penetration depth between 50 and 110 μm. Therefore, the consolidating effectiveness, as assessed by the measurement of the stone hardness and UPV propagation is found nearly absent in the stone. However, the nanoparticle accumulation does not act as a barrier against the water absorption by capillarity, nor against the vapour transfer.

The stone substrate, the product amount and the treatment procedure replicated those adopted in a previous study, where silica nanoparticles were used in a water dispersion. Better treatment performances in terms of penetration depth and consolidationg effectiveness were obtained when water was used as dispersion medium. The poor penetration of colloidal nanosilica in alcohol is probably due to the back migration of the nanoparticles during drying, with a consequent accumulation beneath the surface.

Finally, the study contributes to understand the transport and deposition mechanisms of nanosilica within porous materials. The solvent, which plays an important role on the kinetic stability of the dispersion, is one of the main parameters to be addressed in order to improve the precipitation of nanoparticles in depth.

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Complexities in comparing UPV data over a >30-year exposure trial of consolidated sandstone

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SUMMARY: Complexities in comparing UPV data over a >30-year exposure trial of consolidated sandstone.

KEY-WORDS: long-term weathering; long-term performance; non-linear weathering; stone exposure-lag-response

1. INTRODUCTION

Numerous stone-built heritage monuments around the world have been treated with chemical conservation agents (consolidants) to prolong their life span. To determine the actual extension of life span, however, it is necessary to assess the long-term performance of these consolidants. This is difficult because 'untreated' building stone may take decades to respond to the environment through degradation and weathering (e.g. Meierding 1993; de Wit et al. 2015), a lag that is likely to be extended for consolidated stone materials. This period of time exceeds all laboratory experiments on stone weathering and most of the long-term outdoor exposure trials. In long-term weathering the variability of the environment is combined with accumulated weathering stress over time, cause complex stone behaviour as multiple (opposing) material responses like crust forming and surface recession compete, resulting in non-linear behaviour that is difficult to predict (e.g. Kucera et al. 2007; Přikryl 2013; Viles 2013). Nevertheless, the few well-documented long-term outdoor exposure trials provide invaluable insights into long-term performance of stone consolidants because they account for both accumulated weathering (stress) history and long-term weathering environment variability (e.g. von Plehwe Leisenet al. 1996 a,b; Raupach and Brockmann 2001; Moreau et al. 2008). One such example is the 'Stone Deterioration and Stone Conservation' project, a former large-scale interdisciplinary exposure trial between 1986-1996 funded by the Ministry for Research and Technology in Germany (BMFT, now BMBF). For more than 30 years, large specimens known as 'Asterixe,' (singular 'Asterix') with complex geometries that mimic architectural characteristics with varying levels of exposure (unsheltered) such as slopes and protruding cornices as well as sheltered areas (beneath the cornices and incisions; Fig. 1 and 4), have been exposed to known outdoor environmental conditions.

This unique archive and scientific resource (Snethlage 2005) has been revived recently by the Built Heritage Research Initiative (BHRI), a collaboration between the Getty Conservation Institute (GCI), the Oxford Resilient Buildings and Landscapes Lab (OxRBL) at the University of Oxford, and the Fraunhofer Institute for Building Physics (IBP; Wilhelm et al. 2020).

In November 1995, during the final phase of the BMFT project, five Ihrlersteiner Asterixe specimens after about 10 years of outdoor exposure were treated with two consolidants, a hydrophobic silane modified polyurethane prepolymer (Co. Bayer Leverkusen; solvent n-Butylacetat; solid matter 25w%) and a non-hydrophobic epoxy based resin (solvent Methylisobutylketon; solid matter 21w%). The latter (as one of the few remaining treated specimen) is the focus of this study which aims to compare the data collected in 1995 with that collected in 2019 as different equipment and methods were used for Ultrasonic Pulse Velocity (UPV) to investigate treated and untreated Ihrlersteiner sandstone Asterixe after 30 years of outdoor exposure.

Figure 1. Holzkirchen (Germany) March 2019, outdoor test site with a selection of Asterixe specimen with the front facing West and the South side facing the Alps (middle foreground: Asterix No 4 was part of this study; ©Wilhelm 2019).

2. MATERIAL AND METHODS

The Ihrlersteiner Sandstone (also known as Regensburger Green Sandstone) is a green to green-brown, fossiliferous sandstone (Cenomanian, Upper Cretaceous). This stone type is characterised by a high natural variability and the literature distinguishes 3 to 7 varieties (cf. Mausfeld et al. 1990; Meinhardt-Degen 2007; Poschlod and Wamsler 2009; cf. Table 1). Both the stratum of origin and orientation of the bedding determine the weathering behaviour which is classified as poor to moderate (Grunert and Szilagyi 2010).

Table 1. Stone properties Ihrlersteiner Green Sandstone showing high natural variability (Grimm 1990; Szilagyi 1995; Behlen et al. 2008; Grunert and Szilagyi 2010; Wiese et al. 2012).

Ihrlersteiner sandstone	
Density (bulk/raw)	2.13 – 2.35 g/cm³
Porosity	11.00 – 20.6Vol%
Water uptake atmos	3.33 - 5.84 M% parallel to bedding 2.39 - 3.65 M% perpendicular to bedding
Specific surface	7.20 m²/g
Water absorption coefficient	0.2 – 1.4 $kg/m^2\sqrt{t}$
Compressive strength (UCS)	Average 40.72 MPa (36.6-46.8 MPa*)
Bending strength	3.2 MPa

Prior to the consolidation in 1995 the Asterixe had been exposed for about 10 years to an Alpine climate in Holzkirchen (i.e. high precipitation and freeze-thaw cycles in winter as well as warm and sunny summers with a low concentration of pollutants; cf. Mansch et al. 1999). In 1995 the Asterixe were cleaned (sand blasted) and both Ultrasonic Pulse Velocity (UPV) and water uptake (Karsten tube Ø 50 mm) were measured before and after the consolidation treatment. A gamma probe was also used to determine the depth of the consolidant penetration, which ranged between 23 to 33 mm. This range of depth is well within the margins suggested by Snethlage and Sterflinger (2014) for stones with a capillary uptake coefficient (w-value) < 2 kg/m$^2\sqrt{t}$.

The UPV surface velocity (Raleigh wave or refraction method) was measured which is beneficial when the area of interest is accessible from only one side (e.g. Ahmad et al. 2014). Yet, whether the measurement was made parallel or perpendicular to the bedding is unknown; a crucial information for a stone type with a high level of anisotropy (Siedel and Siegesmund 2011). Further, the only archival information we have on the historically used transducer/receiver pair is that they covered a frequency spectrum of 50–150 kHz and were designed specifically for dry coupling.

In October 2019 the UPV method in this study was based on Wilhelm et al.'s approach (2020; illustrated in Fig. 2) and focused on three Ihrlersteiner Asterixe (No 4, 8, 9), one of which (No 4) had been consolidated in 1995.

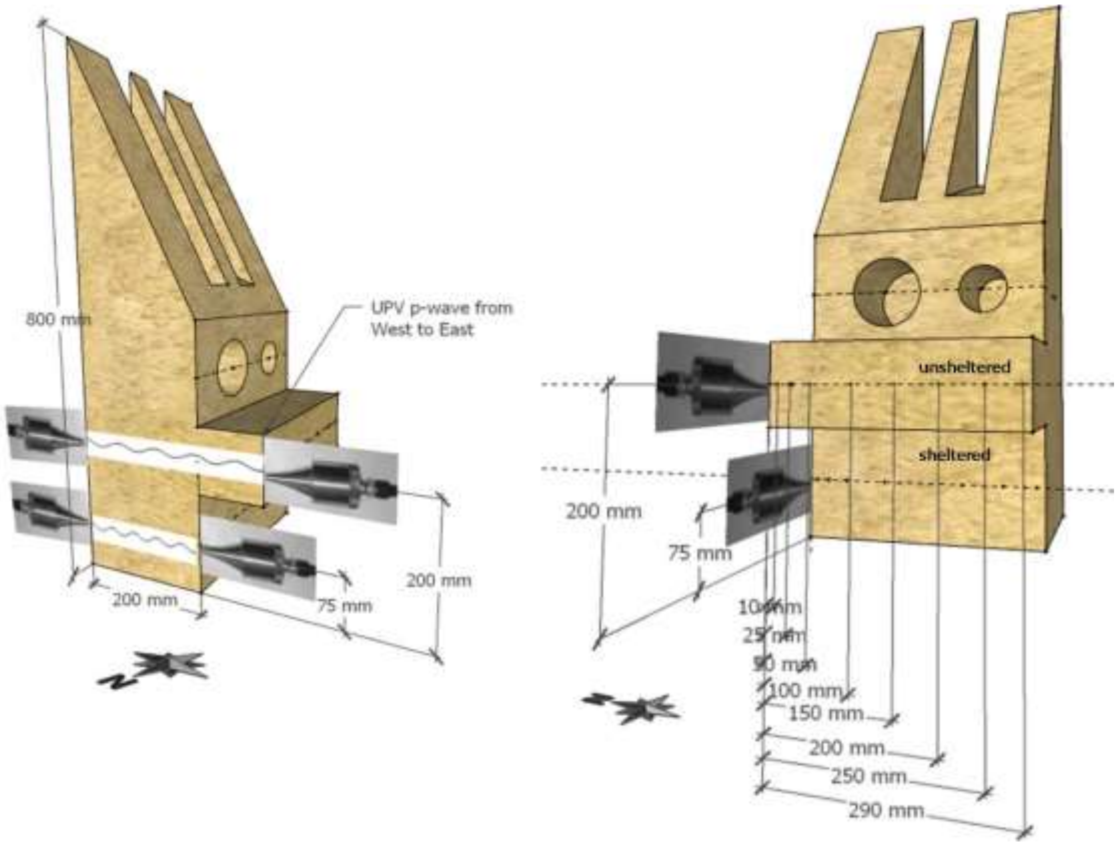

Figure 2. UPV measurements method with planes at 2 heights (75 and 200 mm from the base) and the p-wave travel direction from West to East. In total 9 sets of measurements (30 readings each) per plane were conducted with moving the transducers in incremental steps from left (northward) to right.

The Pundit Lab(+) Proceq© with an exponential transducer/receiver pair (54kHz) and an elastomer as couplant was used to acquire UPV data for planes ('cross sections') at two different heights in an unsheltered (cornice) and sheltered area (beneath cornice) of each Asterix (75 and 200 mm from the base respectively) with the p-wave (V_p) running from West to East parallel to the bedding. In total 9 sets of measurements (30 readings each) per plane were conducted while moving the transducers in incremental steps from left (northward) to right (southward). The measurements were complemented with microwave measurements for material moisture using the MOIST350B device (hf sensor; Leipzig, Germany) with probe R with up to 3cm and probe D with up to 10 cm of penetration depth. The device operates in the microwave frequency band around 2.45 GHz and thus, is not affect by potential salt content in stone (cf. Maierhofer and Woestmann 1998; Orr et al. 2019). The device measures the reflection coefficient, the proportion of reflected energy from an applied electromagnetic wave and is reported in this study as unitless moisture index (MI), an arbitrary unit related to the reflection coefficient. Both probes were applied on all four aspects on the area below the cornice with a measuring grid of 9 x 5 (2 x 45 measurements per aspect surface, Fig. 3).

The on-site approach was complemented with a laboratory study on weathered Ihrlersteiner specimen correlating the direct and the indirect UPV method, and investigating the effect of material moisture on UPV measurements with the specimen being conditioned in a climate chamber at two distinctly different relative humidities, 20% and 80% RH at a constant temperature of 20°C. The data obtained was mainly non-normally distributed as is common for weathered stone (Shapiro Wilk test sign. level p-value<0.05; cf. Mosch and Siegesmund 2007; Wilhelm et al. 2016). Therefore, the programme R Studio was used for non-parametric statistical analysis.

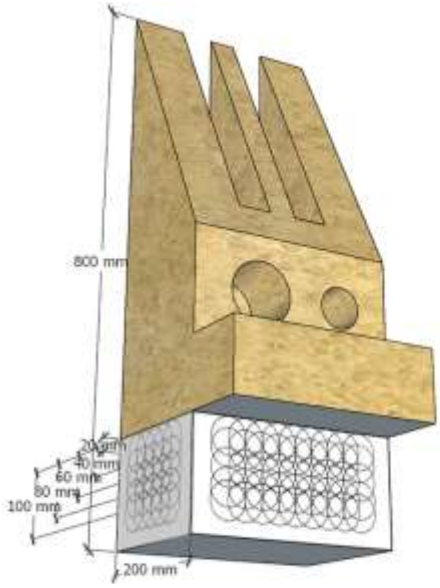

Figure 3. MOIST350B measuring grid of 9 x 5 measuring points per aspect for probes R with up to 3cm and D with up to 10 cm penetration depth.

3. RESULTS AND DISCUSSION

This study observed common stone weathering patterns such as differential erosion (rounding and roughening), granular disintegration, fragmentation (the top pinnacles are particularly prone), biocolonisation and for Asterix No 4 crack formation (e.g. Grimm 1990; Behlen et al. 2008; Verges-Belmin 2008). The absence of scaling indicates that the consolidant was successfuly applied with sufficient penetration depth and without a sharp transition zone between outer area and the core of the specimen; thus, not caused any secondary damage as might be observed with shallow penetration depth of consolidants (e.g. Meinhardt-Degen 2005). Overall, the material surface characteristics of the Asterixe have become more heterogenous and all (including the consolidated one) follow a similar trend of differential weathering according to the main weathering direction (South-West) and in relation to the complex geometry of the specimen. Figure 4 shows examplary soiling patterns observed on all investigated Asterixe specimen in this study. Different water run-off regimes result in less soiling on the East exposed side beneath the incision which slopes westward (to where it guides the water) versus the area below the incision that does not slope (horizontal orientation) exhibits darker soiling as water flows off equally on both sides (East and West). Further on the East exposed side in a narrow zone following vertically the south- and northward edges, noticable biological growth (lichens and biofilm) can be observed, indicating a beneficial balance between light and water supply. Similarly, the sloped top of the west-facing side also appears to have favourable circumstances for biological growth such as mosses and lichens.

For the unsheltered cornices and the sheltered areas underneath the cornices the archival records state that the protruding cornices experienced higher rates of moisture variations as on the one hand more water accumulates on top of it which on the other hand evaporates more rapidly because of the benefical volume:surface ratio (Hoyer 1997, p 3). In contrast, the area below the cornice will have expierenced a different moisture regime as the cornice sheds rain and water run-off from it. Yet, evaporation might be slower and result in extended periods of higher material moisture as the volume:surface ratio is less beneficial compared to the cornice which further might partially block the sun (as can be seen in Fig. 1 and 4). In this study we observe for the sheltered areas right beneath the cornices (crescent shaped) the least surface changes, with neither obvious soiling nor visible biological growth. This demonstrates the crucial role of cornices in mediating environmental weathering agents such as particulate matter deposition, wind driven rain and water runoff (e.g. Wood 1993; Mulvin and Lewis 1994; Blocken et al. 2013; Wilhelm et al. 2020).

Figure 4. Asterix No 9 (non-consolidated) in 2019, from left to right: sides exposed to South (Alps), West, East and North. The East side shows a differentiated soiling pattern following the two different water run-off regimes facilitated by the different geometries of the incisions where the one on the left (southward) slopes towards West and the one on the right has a horizontal base.

To arrive at a proxy comparison for the historic and the recent UPV data, a multistep procedure of data conversion was pursued as both different types of UPV transducers (standard cylindrical and exponential concial) and application methods (direct and indirect) are not directly comparable. Lee et al. (2017) find that different UPV transducer types and application methods yield different results and determine for Boryeong sandstone a mean correction factor for the direct method of 1.08 (fresh stone) and 1.59 (artificially weathered stone) and for the indirect method a factor of 1.58 for exponential transducers (5mm diameter, 54 kHz), as used in this study, to standard transducers (50 mm diameter, 54kHz).

In addition, our study experimentally defined on a weathered Ihrlersteiner sandstone a conversion factor of 1.23 for the exponential transducers (5mm diameter, 54 kHz) to the standard transducers (50 mm diameter, 54k Hz) and a factor of 1.48 from the direct to the indirect method. Similarly to Lee et al. (2017) we find the results generated through the exponential transducers and the indirect method to be lower compared to the standard transducers and the direct method.

However, when we apply the conversion factors for the indirect method (1.48, 1.59) to the historical data, we achieve mean (median) and maximum values which are considerably higher V_p (e.g. 4047 (4083) m/s and 5374 m/s respectively) than is generally reported for fresh Ihrlersteiner sandstone (e.g., Meinhard-Degen (2005) reports V_p 2800–3700 m/s for four Ihrlersteiner varieties; cf. Table 2). This raises the question of whether the historical data has been transformed from the indirect to the direct V_p without specifically reporting it. Yet, when we compare the non-converted historic values to the highest V_p of the recent study (i.e. most intact stone fabric and converted to standard transducers with factor 1.23) we find for the Asterixe No 8 and 9 (non-treated) V_p 3030 m/s and 3234 m/s respectively which are higher than the historic mean of V_p 2980 (median 2920) m/s (cf. Table 2 and Fig. 5). However, we have no reason to believe that the Asterixe specimen might have hardened over time to explain the higher V_p after 30 years of exposure. Therefore, another uncertainty for field measurements needs to be considered with potential moisture gradients likely to have affected the UPV measurements. At the time of the historic UPV measurements in November 1995 the specimen had been conditioned for weeks in a workshop with a frost-free but uncontrolled room climate. Consequently, high relative humidities (RH%) are a possibility following outdoor climatic trends between 50 – 95%RH. Initial results from our ongoing laboratory study showed that the Ihrlersteiner specimen exhibit higher V_p (~20%) when conditioned under 20°C and 20% RH compared lower V_p after 20°C and 80% RH conditioning. This shows that we cannot confidently compare the data of our recent study with the historic data unless we are able to calibrate our UPV method to unweathered samples (such as drill cores) of the exposed Asterixe (cf. Bourges 2006).

Table 2. Comparison of Ihrlersteiner Asterixe (indirect) Vp results from surface measurements in 1995 after 10 years of exposure and before and after consolidation with converted values using two conversion factors, 1.59 (Lee et al. 2017) and 1.48 (this study).

Specimen condition	Exposure period at time of treatment [years]	Mean (Median) V_p [m/s]	Mean (Median) V_p [m/s] with conversion - factor 1.48	Mean (Median) V_p [m/s] with conversion - factor 1.59
Naturally weathered substrate after cleaning and before consolidation	10	2980 (2920)	4047 (4083)	4345 (4373)
Naturally weathered substrate after cleaning and after consolidation	10	3980 (3950)	5381 (5217)	5781 (5605)

Only for Asterix No 4 (consolidated) is the max V_p of this study with 3497 m/s lower than the historic V_p mean V_p after consolidation with 3980 (median 3950) m/s. This potentially could reflect real-world behaviour, with V_p decreasing with time, implying that the original V_p gain of 1000 m/s through consolidation has been reduced by 500 m/s. Asterix No 4 also exhibits the lowest V_p values of this study (327 – 834 m/s) which is indicative of structural disintegration around a visible crack (Fig. 1). However, the fact that the consolidated Asterix has the most intense change in material properties and pronounced weathering may not only be due to the 1995 consolidation, but also due to the inherent variability of the Ihrlersteiner sandstone and cumulative effects, as we have seen other untreated Ihrlersteiner Asterixe that have weathered similarly. It is further possible that the historically most weathered Asterixe were selected for consolidation. Thus, we might cautiously conclude that the consolidation prolonged their life span but further research is needed to understand how the different consolidated and non-consolidated varieties of Ihrlersteiner sandstone (or any sandstone with high inherent natural variability) respond to long-term weathering impacts.

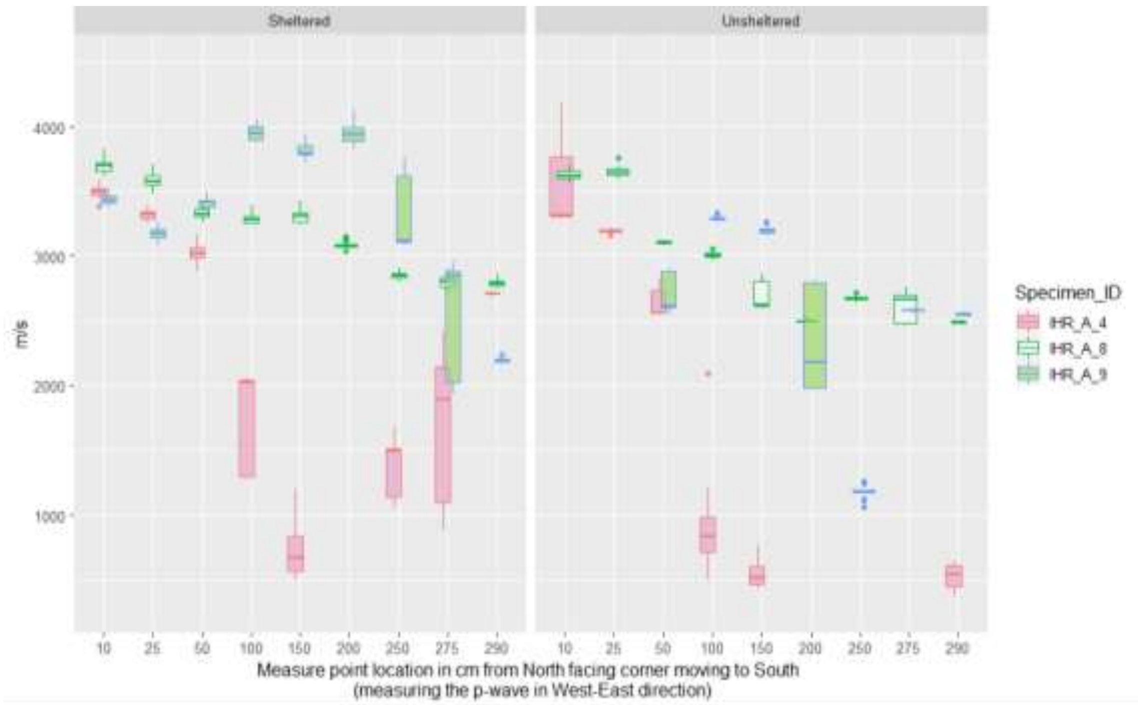

Figure 5. Boxplots of in-situ UPV measurements of the Ihrlersteiner Asterixe No 4 (consolidated), 8, and 9 (non-consolidated). The x-axis marks the distance of the measuring points starting at the North end of the specimen (10 mm) moving towards the South (290 mm). The p-wave travel direction was from West to East (cf. Fig. 2).

The UPV results can still be compared relative to each other, providing useful insights into material property changes. We observe lower V_p on the southward section (closer to the Alps) of the west-facing side and higher V_p on the northward section indicating a gradual material change (Figure 5). Further, the sheltered areas (beneath the cornice) exhibit higher V_p (median range of meas point at 10 mm = 3319 - 3697 m/s) and less data spread compared to the unsheltered areas (cornice; median range of meas point at 290 mm = 542 – 2789 m/s; cf. Fig. 2 and 5).

The archival records from 1997 (Hoyer 1997, p 9) state that the area and core below the cornice shows lower material moisture compared to the cornice area. As a consequence, the area underneath the cornice experiences less weathering stress which is reflected in the higher V_p for the marjority of the measured areas (the exception being Asterix No 4 with the above mentioned crack and structural disintegration). The records state further, that the northward exposed sides exhibit lower material moisture compared to the southward exposed sides (Steiger et al. 1996, p 25). Yet, the MOIST350B results in our study indicate an opposite trend with the northward sides showing higher moisture indices compared to the southward sides for Asterix No 4 and 8 (Figures 6 - 9). Considering the moisture effect on UPV measurements discussed above we might expect for the damper areas (northward sides) of the Asterixe specimen to result in lower V_p and vice versa. Instead we find that the northward areas exhibit higher V_p in comparison to the southward sides. However, results should be interpreted with caution as Orr et al. (2019) find that uneven distribution of material moisture might effect the moisture index results and over- or under-estimate the reflection coefficient.

Similar to the UPV measurements, further calibration and and correlation of non-destructive methods and respective data processing is required to better understand the complex system interactions of long-term consolidation performance with outdoor climate variability, and heterogenuous stone weathering behaviour.

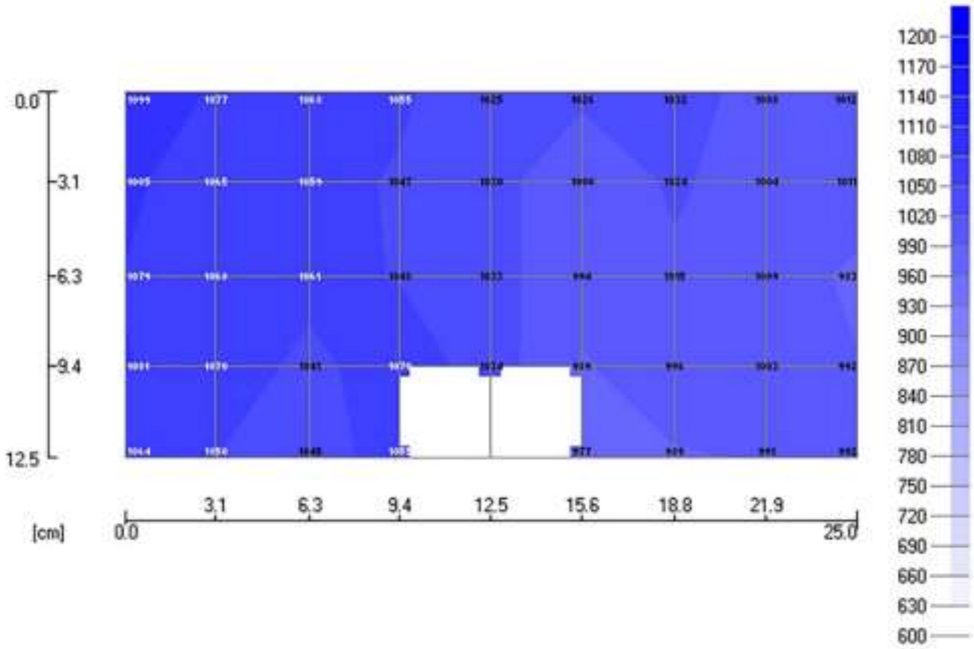

Figure 6. Ihrlersteiner Asterix No 4 (consolidated), West exposure (northward section to the left and southward section to the right), MOIST350B moisture index map up to a depth of 3 cm where a darker blue indicates a higher moisture index (cf. Fig. 3).

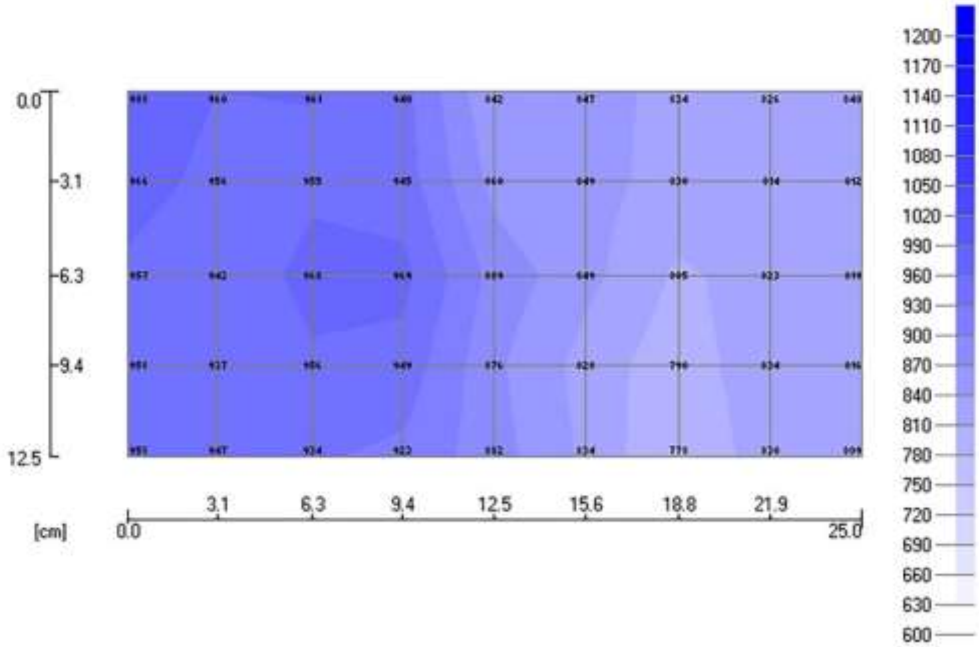

Figure 7. Ihrlersteiner Asterix No 4 (consolidated), West exposure (nortward section to the left and southward section to the right), MOIST350B moisture index map up to a depth of 10 cm where a darker blue indicates a higher moisture index (cf. Fig. 3).

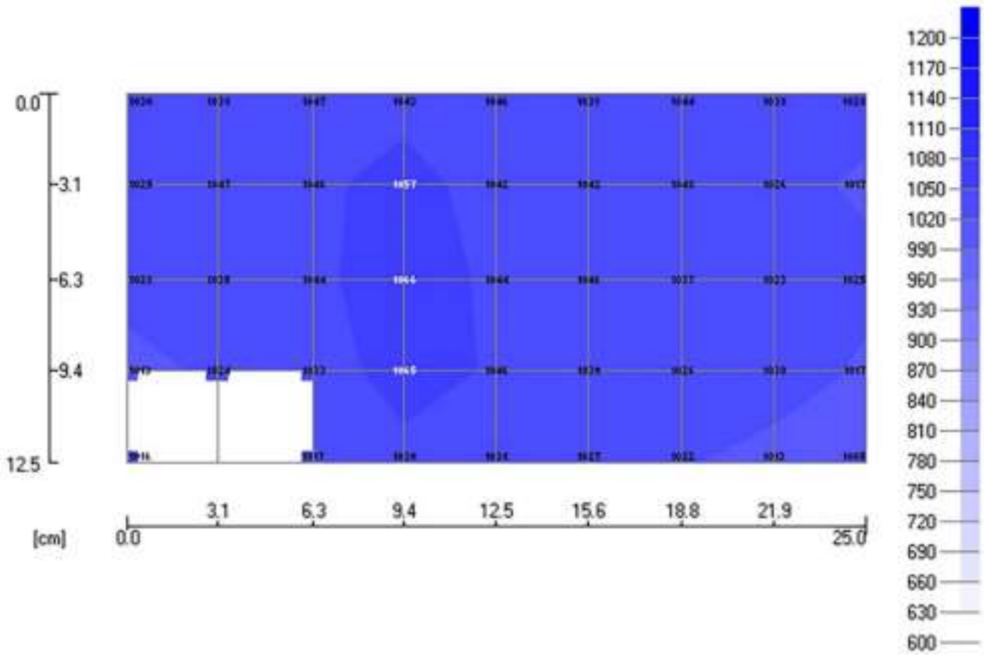

Figure 8. Ihrlersteiner Asterix No 8 (non-consolidated), West exposure (nortward section to the left and southward section to the right), MOIST350B moisture index map up to a depth of 3 cm where a darker blue indicates a higher moisture index (cf. Fig. 3).

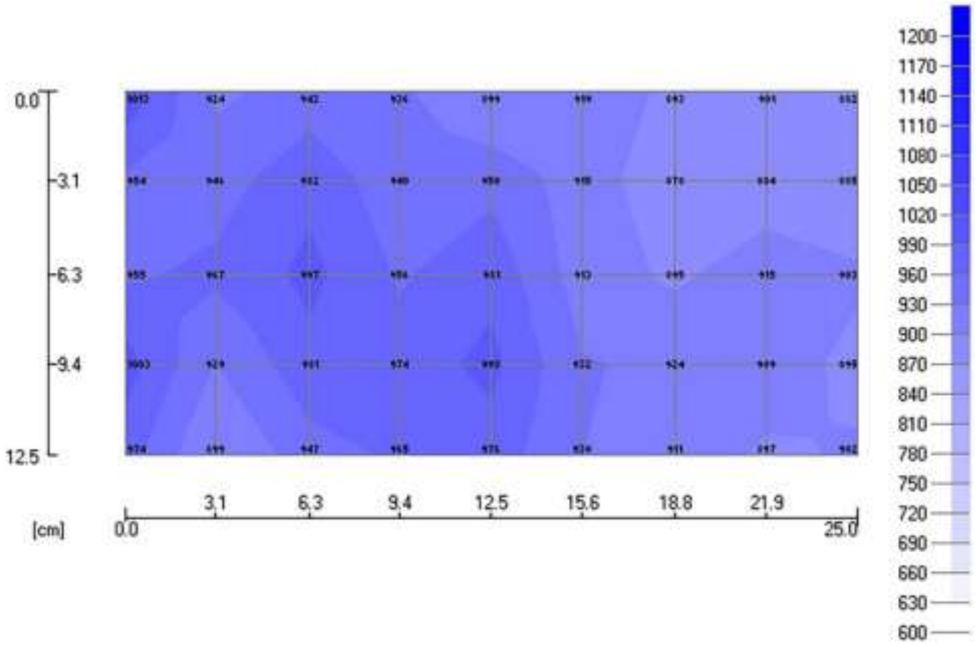

Figure 9. Ihrlersteiner Asterix No 8 (non-consolidated), West exposure (nortward section to the left and southward section to the right), MOIST350B moisture index map up to a depth of 10 cm where a darker blue indicates a higher moisture index (cf. Fig. 3).

4. CONCLUSION AND OUTLOOK

This paper sheds some light on the complexities encountered when trying to evaluate the efficacy of long past sandstone consolidation on naturally exposed specimen. Not only is the uncertainty of the results related to the inherent variability of the tested stones which increases with extended exposure (e.g., Mottershead 2000), but the incomparability of former methods and equipment adds further uncertainty. To reduce the uncertainty, encourage complex system evaluation and ensure the value of this long-term exposure trial beyond its more realistic presentation of real-world long-term stone weathering behaviour it is planned to complement the non-destructive characterization and perform laboratory investigation on collected samples.

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The evaluation of stone deterioration state using non-destructive techniques on a medieval fortress in Syria.

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SUMMARY: Crac Des Chevaliers is a significant crusader castle that was built over a long period of time using a variety of stone lithotypes and building techniques. The age of this edifice combined with the geographical and environmental conditions implies a wide range of stone deterioration types, such as biological colonisation, salt crust, discoloration, fragmentation, exfoliation, cracks, and loss in stone material. According to the deterioration mapping results, the types of stone deterioration are associated with the orientation and location (inside or outside the building).

Non-destructive techniques were used to assess the stone deterioration state at the castle (water absorption test by Rilem tube and Schmidt hammer). The water absorption rates of the stones differed according to the type and severity of stone deterioration. The Schmidt hammer results revealed that the stones have varying compressive strengths, where the lower value of compressive strength was for mechanically damaged stones.

KEY-WORDS: Non- destructive techniques, Rilem tube, Schmidt Hammer, Deterioration mapping, limestone

1. INTRODUCTION

Crac Des Chevaliers is a remarkable medieval fortress in Syria. It is a combination of Crusader and Islamic architectural ruins since the 12th-13th century (Mesqui-2018, Goepp & Mesqui-2018). This unique structure, registered in the world heritage list since 2006, was basically built from carbonate stone blocks on a basaltic foundation and suffers from serious issues that require urgent intervention. According to Köppen's classification, the region of the castle is characterised by a Mediterranean dry hot summers climate (CSA) (Peel et al.-2007). The summers are warm to hot- dry, and the winters are mild- wet (Faour & Meslmani - 2010). In winter the temperature can drop down to freezing degrees (Bilal & Rozgonyi-2020). Due to the long construction phase, the stone blocks with different porosity and structural properties were built together. These varieties in pore structure lead to diversity in moisture content (Franzen & Peter-2004, Charola, & Wendler-2015); and decay types (Török & Rozgonyi-2004, Lindqvist-2007) such as salt crystallisation (Buj & Gisbert-2010, Alves, et al.-2011) and biological colonisation (Crispim & Gaylarde-2005) on the stone surface as well. In addition to the decay of the stone structure, there are aesthetic issues that challenge our heritage buildings. One of these issues is the colour alteration (discoloration) of the masonry. Rivera et al. (2018) emphasised that discoloration might be derived from solar radiation that can chromatically alter the stone surface because of UV radiation effect (Navarro et al.- 2019). Moreover, gypsum formation (Lee & Araki-2019), presence of iron oxides in stone minerals (Zha et al.-2020), exposure to fire or high temperatures (Ozguven & Ozcelik-2013), and biological attacks (Cutler et al.-2013, Prieto-2007) are also causes of colour change of stone masonry.

The primary assessment of the stones weathering state is usually fulfilled by non-destructive techniques, which include investigating the decay cases and drawing deterioration maps in situ. The deterioration mapping is a field study that relies on labelling visible weathering cases, i.e. (mm-cm-m) (Fitzner & Heinrichs 2002). The outcome of deterioration mapping provides a general view of the most common types of decay as well as the deterioration condition of the building (Brunetaud et al.-2012). However, this technique is insufficient unless it is followed by an analytical study of the stone deterioration types to deduce the weathering mechanism of each (Rodrigues 2015).

The concept of using non-destructive techniques to determine the extent of damage in historic buildings stems from the fact that stone blocks cannot be removed from these structures, making testing and assessing their properties and conditions difficult (Valero et al.-2019). Therefore, utilising these techniques in historic buildings could be helpful either in assessing the deterioration degree (Fais et al.-2018) or in evaluating the treatment or restoration work (Livingston-1999). One of these techniques is the water absorption test with Rilem tube, where the capillary water absorption ability of the stone surface is measured. This tube was developed to evaluate the capillary uptake of rainwater carried and directed by the wind. The pressure of 100 mm height of the water column is equivalent to the wind pressure of approx. 160 km/h by rain (Vandevoorde et al.-2009). The use of the Schmidt hammer in historic buildings is a common technique to predict the compressive strength property of the stone (Katz et al.-2000) or estimate the stone weathering or preservation state (Török-2003). Many studies have been conducted to predict compressive strength using the Schmidt hammer measurement (Miller- 1966, Buyuksagis & Goktan-2007, Rajabi, Ali M. et al. -2017, Aliabdo-2012, Oyediran-2018).

This article will present the Rilem tube penetration test and the Schmidt hammer rebound test for different types of stone deterioration and lithotypes at Crac des Chevaliers. In addition, two deterioration maps of the north and east external façades will distinguish the types of stone deterioration and their distribution. The results mentioned in this work are the outcome of the field investigations before taking samples to the laboratory.

2. MATERIALS

The castle was built mainly of carbonate stones (limestone, dolomitic limestone and dolomite (Al-Khateeb, 2008). It is challenging to distinguish these stone types on the site, so they are called carbonate stone by collective name. By the field investigation, the carbonate stones were categorised into four lithotypes as follow: 1) homogenous porous stones (HPS); 2) homogenous dense stones (HDS); 3) laminated stones (LS); 4) newly built stones (NBS). HPS is a homogenous carbonate stone with visible porosity, where its pores size range between 0.5 mm to 2 cm. HDS is a homogenous dense stone whose porosity is not visible to the naked eye. LS is a laminated carbonate stone where the sedimentary layers appear clearly on its surface with 10-20 cm in height. In some laminated stones, big flint particles can be found parallel to the sedimentary layers; and the size of the flint particles ranges from 3 to 10 cm (Figure 1). NBS are the stones brought to the castle from nearby quarries for restoration work. These newly built stones were rebuilt during the restoration work between 2002 and 2004. HDS and LS are more common at the castle compared with HPS. The percentage of newly built stone is very low. Some HPS and NBS types stones could be found without any decay; however, non-weathered stones of HDS and LS types could not be found at the castle.

Figure 1 The lithotypes of carbonate stones used in Crac des Chevaliers.

3. METHODS

3.1 Deterioration mapping

Two deterioration maps were created for facades belonging to the Building (36) facing different directions: 175 m^2 external eastern façade (F1) and 107 m^2 external northern façade (F2), as shown in Figure 2. The building is located on the southern side of the internal castle on the first floor. It is a two-storied building whose plan is a semi-rectangular shape with an approximate area of 148 m^2. It was built by dolomite stone blocks whose height ranges from 50-60 cm, and their width is variable (30- 170 cm). This building is bounded directly from the east by Building (35) on the first floor, so it only has an outer east façade on the second floor. In comparison, façade (F2) consists of two stories. The height of the façade is approximately 16 m, whereas its width is approximately 13 m.

3.2 RILEM tube penetration test

In this study, the tube was filled once only in each test, so the water pressure applied by the water column inside the tube was decreasing over time. As a result, the stone was not exposed to constant water pressure during the test. According to (Balakrishna et al.-2013), the differing in water pressure simulates the actual condition of the building in which it is not exposed to a constant wind speed.

Rilem tube penetration test exhibited different kinds of water absorption behaviour of the stones depending on the following conditions: i) stone lithotype, ii) type and the intensity of stone deterioration, iii) position of the stone blocks (indoor or outdoor).

3.3 Schmidt hammer rebound test

The preservation of building materials is a high priority in historic buildings therefore the low energy "L" type of Schmidt hammer (0.735 J impact energy), which is used for stones and bricks, is typically used. (Aydin & Basu 2005).

In this investigation, the "VSYIQI" HT-75 brick rebound hammer was used. The measurement was made horizontally on the vertical stone surface. On each tested stone surface, min. 20 measurements on different measuring points were performed. A statistical study was conducted to identify and eliminate outlier values and calculate the average and standard deviation. The statistical study was carried out using the "PASW Statistics 18" software. The stones, which were tested by Rilem tube, were also tested with Schmidt hammer. (Buyuksagis & Goktan-2007) conducted different equations to calculate the compressive strength from the rebound value. Each equation was associated with a specific measurement procedure and a Schmidt hammer type. One of these equations (equation [1]) was obtained by using the "L" type Schmidt hammer. The rebound value was calculated by omitting the outliers before averaging the remaining measurements. In this study, the compressive strength of the tested stone was calculated from equation [1].

$y = 3.6834e^{0.0679x}$ equation [1];

where y is the uniaxial compressive strength in [MPa] and x is the rebound value measured on a horizontally stone surface.

While the Schmidt hammer measurements were made in this study horizontally, the measured values were corrected (Barton & Choubey-1977) before using of equation [1].

4. RESULTS AND DISCUSSION

4.1 General overview of stone decay cases at the castle

The most serious issues at the castle can be defined as:

i) Damaged stone blocks result from the recent armed conflict in Syria. These stones have different intensities of damage: Demolished stone blocks cannot be restored because they are too fragmented and must be replaced (Figure 3a). Stones exposed to a direct bullet that left powdering of the stone material (Figure 3c) and stones exposed to missile fragments which lead to a loss in stone material (Figure 3b), are still restorable in most cases. The pitted and rough surfaces of the outer façades from the shots represent a favourable environment for the flourishing of various species of microorganism colonisation.

ii) The growth of invasive plants, especially the presence of shrubs, influence the stability of the whole wall. The herbaceous species are widespread between stone joints or even inside the stone cracks (Figure 3d). The pitting of the stone surfaces is a typical case in the castle. Higher plants and herbaceous species contribute to chemical deterioration of the stone surface by their respiration process resulting in acidic erosion (pitting) caused by carbonic acid production (Jain et al. 1995). (Figure 3h).

iii) The colonisation of microorganisms on both the exterior and interior walls can be observed to a large extent. The ambient environment of the castle is favourable for flourishing many kinds of microorganisms. Three colours caused by biological colonisation are the most characteristic in the castle: grey stone surface due to the deposition of grey microorganisms (Figure 2e), red-orange coloured stone surfaces (Figure 3i) and green coloured stones (Figure 2f). Grey microorganisms are concentrated on the western and northern external facades covering significant parts of the facade. They are present in southern and eastern facades on the areas shaded with plants. The red-orange microorganisms are concentrated on the outside damped stone surfaces, which does not receive much sunlight. Even in the summer, they are common on the external northern facades and any moistened area that allows these microorganisms to thrive all year at the castle. The green microorganisms are presented in the internal facades with enough moisture to flourish. Many of the castle towers suffer from water infiltration in the walls that mainly occurred as a side effect of the bombing and led to the dense presence of green algae on the inner walls (Figure 3f).

iv) Salt efflorescence is not only present on the ground floor level because of rising damp; but also at the level of the upper floors where those salts appear in light thickness (Figure 3j). One of the possible sources of salts is the air bearing sea salts because the castle is located around 35 km away from the coast.

v) The orange discolouration of both eastern and southern façades is a characteristic feature (Figure 3g). In contrast, the shaded areas (e.g., by higher plats) at these façades do not have this discoloration. The orange colour is most likely caused by sunlight. In addition, this colour co-occurs with the scaling under the salt, depending on the stone type (Figure 3k).

Figure 3 Deterioration cases at the castle. a) Demolished fragmented stone. b) stone exposed to missiles fragments. c) Stones exposed to a direct bullet. d) Growing of invasive plants in the joints. e) Deposition of grey microorganisms. f) Green microorganisms on a pillar exposed to water infiltration from the roof. g) Orange discoloration. h) Pitting. i) Deposition of red-orange microorganisms. j) Salt efflorescence. k) Scaling.

4.2 Deterioration mapping

4.2.1 External east façade of Building (36) (F1):

Deterioration mapping of the façade demonstrates various deterioration cases with different percentages (Figure 4 and Figure 5). As mentioned above, the typical stone deterioration case of both façades (F1) and (F2) is orange discoloration. This deterioration is the most dominant on the east façade (37.6%, Figure 4) and is most likely attributed to sunlight exposure; therefore, it concentrates on the entire façade except for the upper quarter where the higher plants have been flourishing and shading the stone blocks formerly.

The deposition of grey microorganisms (approx. 25.5%) occurred in areas shaded from higher plants or on stones with perforations. These perforations are perfect indicators of previous vegetation that formerly shaded these stones. The invasive plants that occupy a place of about 12.65% in this façade are herbaceous species and shrubs. The area of pitting (approx. 1.25%) is typically associated with the presence of plants that cause chemical erosion.

Figure 4 Deterioration mapping of the external east facade of the building (36).

Scaling co-occurs with the presence of discoloration and salt efflorescence. On the orange coloured stone surface appears white salt efflorescence. The percentage of salts efflorescence is 7.45 % (Figure 5) and is concentrated at the lower part of the façade, while exfoliation is 8.89%. This façade is not located on the ground floor where the rising dampness of the soil leads to salt accumulation, instead it is located on the second floor. The source of salts is might be from the mortar between the stones (several stones were replaced in 2004, and inappropriate mortar might have been used) or predominant of the sea spray effect. The east façade is not highly affected by the recent war. Cracks, fragmented and flaking parts resulting from bullets represent a very low proportion of the whole façade (0.33% and 1.11%, respectively).

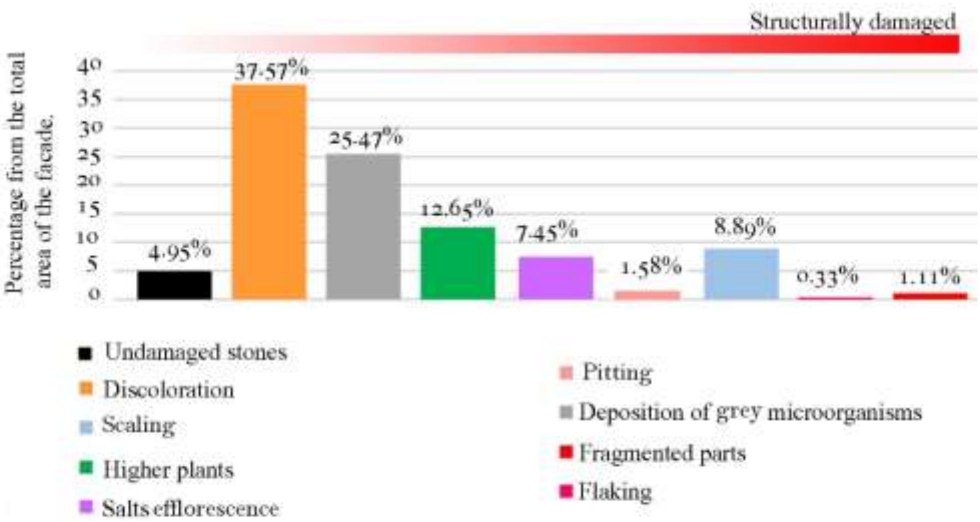

Figure 5 The percentage of each deterioration type at the external east facade of building (36).

4.2.2 External north façade of Building (36) (F2):

Since deterioration mapping is a process that depends on the optical observation and the whole façade is too high to investigate entirely without scaffolding; the deterioration mapping of this façade has been carried out to the lower part of the height.

This façade is distinguished by the appearance of three primary decay forms: deposition of red-orange microorganisms, deposition of grey microorganisms and brown discoloration (Figure 6).

The red-orange microorganisms settled in the mapped area at around 27.8% (Figure 7). These microorganisms can be found in the moisturised shaded sections or areas exposed to low sunlight rates.

Figure 6 Deterioration mapping of the external north facade of the building (36).

The western curtain walls prevent the west and southwest wind from reaching the lower wall section, where these microorganisms spread (Figure 2 and Figure 6). Consequently, the necessary humidity to flourish these microorganisms always exists even in the summer when the wind cannot dry the wall. The upper section of the mapped area can quickly dry by the wind during the summer without any restriction so the deposition of grey microorganisms prevail on it (with approximately 40.67%). A brown discoloration concentrates in the middle part of the mapped area in a percentage of 9.6% (Figure 6 and Figure 7). This façade was also affected by the recent war, where the damaging scale ranges from destroying some parts (the window parts) to the effects of missiles fragmentations. The latter resulted in a loss in stone material (1.72%), fragmentation (1.83%), flaking (0.5%), and cracks in some parts.

The growth of some herbaceous species represents the vegetation (2.75%) in this façade. Since the joints between the stones are very thin, there is not enough space for growing other vegetation such as shrubs or even trees.

4.3 Results of in situ measurements

The homogenous dense stone (HDS, blue colour), the homogenous porous stone (HPS, green colour), the laminated stone (LS, red colour), and the newly built stone (NBS, black colour); with different deterioration types were examined by Rilem tube and Schmidt hammer. According to the availability of deterioration cases at the castle, the stones with the same deterioration type were tested in different lithotypes.

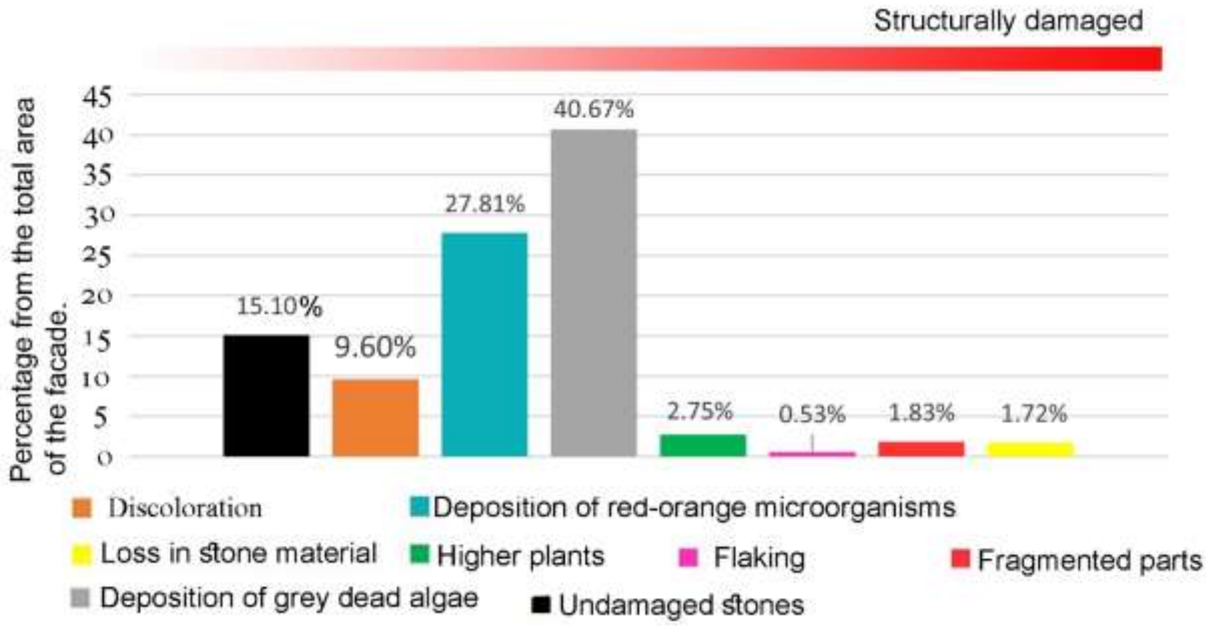

Figure 7 The percentage of each deterioration type at the external north facade of building (36).

The tested stones included four homogenous porous stones (HPS): two without decay (HPS1_0 and HPS2_0), one with salt efflorescence on its surface (HPS_S), and one colonised with microorganisms (HPS_MC).

The physical properties of the homogenous, not weathered porous stones were different. HPS1_0 (Figure 9) was located indoors and revealed a rapid absorption behaviour compared to other tested stones (Figure 8).

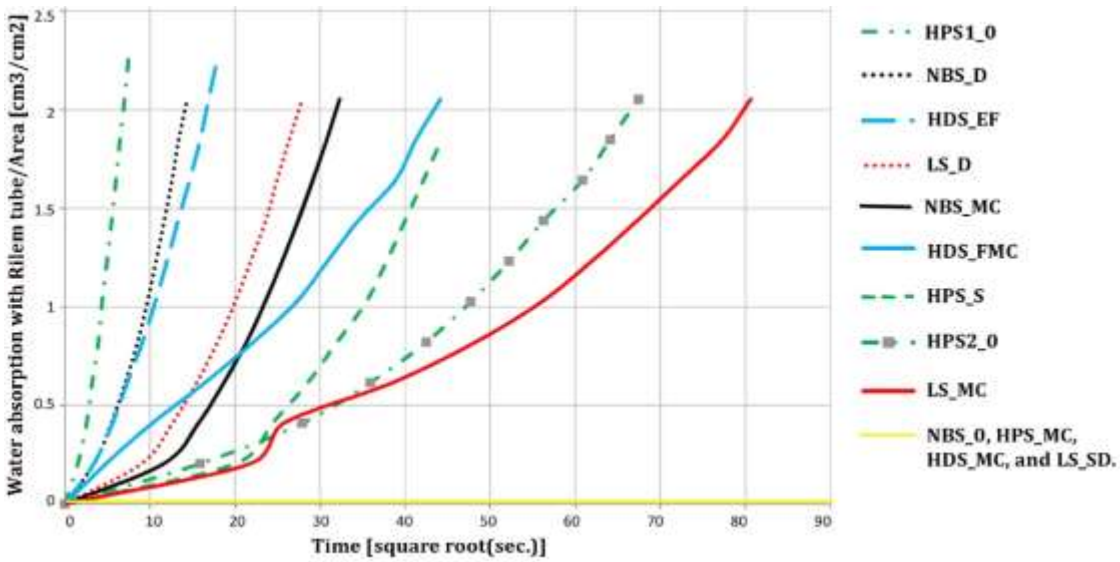

Figure 8 The absorption diagram of the tested stones by Rilem Tube.

The measured rebound value of this stone was 33 (see Figure 10) and its calculated uniaxial compressive strength was 28.5 MPa, see Table 1. Another homogenous porous stone (HPS2_0); with no distinct decay type (Figure 9) was located outdoors about 1 meter above ground on the north external façade of a building on the ground floor level. The absorption rate of the stone was lower (Figure 8) and its rebound value was 6% higher than HPS1_0 (Figure 10), while its calculated compressive strength was 33.7 MPa. The homogenous porous stone with salt efflorescence on its surface (HPS_S, Figure 8) exhibited lower water absorption than HPS1_0 and higher than HPS2_0. Its absorption curve can be divided into two stages in which the absorption rate has changed from relatively low to moderate by approx. 400 sec. The low rate corresponds to the first cubic centimetre of absorbed water, while after that; the absorption rate has increased (Figure 8). The measured rebound value of this stone (HPS_S) was 12% higher than HPS1_0 and higher than HPS2_0 (Figure 10) and its calculated compressive strength was 38.3 MPa. HPS_MC was an outdoor homogenous porous stone colonised by microorganisms and revealed non-absorption behaviour. The measured rebound value of this stone was the highest compared with the other HPS stones: 24% higher than the rebound value of HPS1_0 (Figure 10). As such, the calculated compressive strength of HPS_MC was the highest among the HPS group and it was 49.8 MPa. The absorption behaviours and the rebound values of the two non-weathered homogenous porous stones (HPS1_0 & HPS2_0) were different. It seems that both stones are structurally different, which were reflected in their properties. The rebound values of the HPS were close to each other (about 14% difference in average), but the presence of microorganisms or salt on the stone surface reduced or prevented water from entering the stone and resulted in higher surface strength.

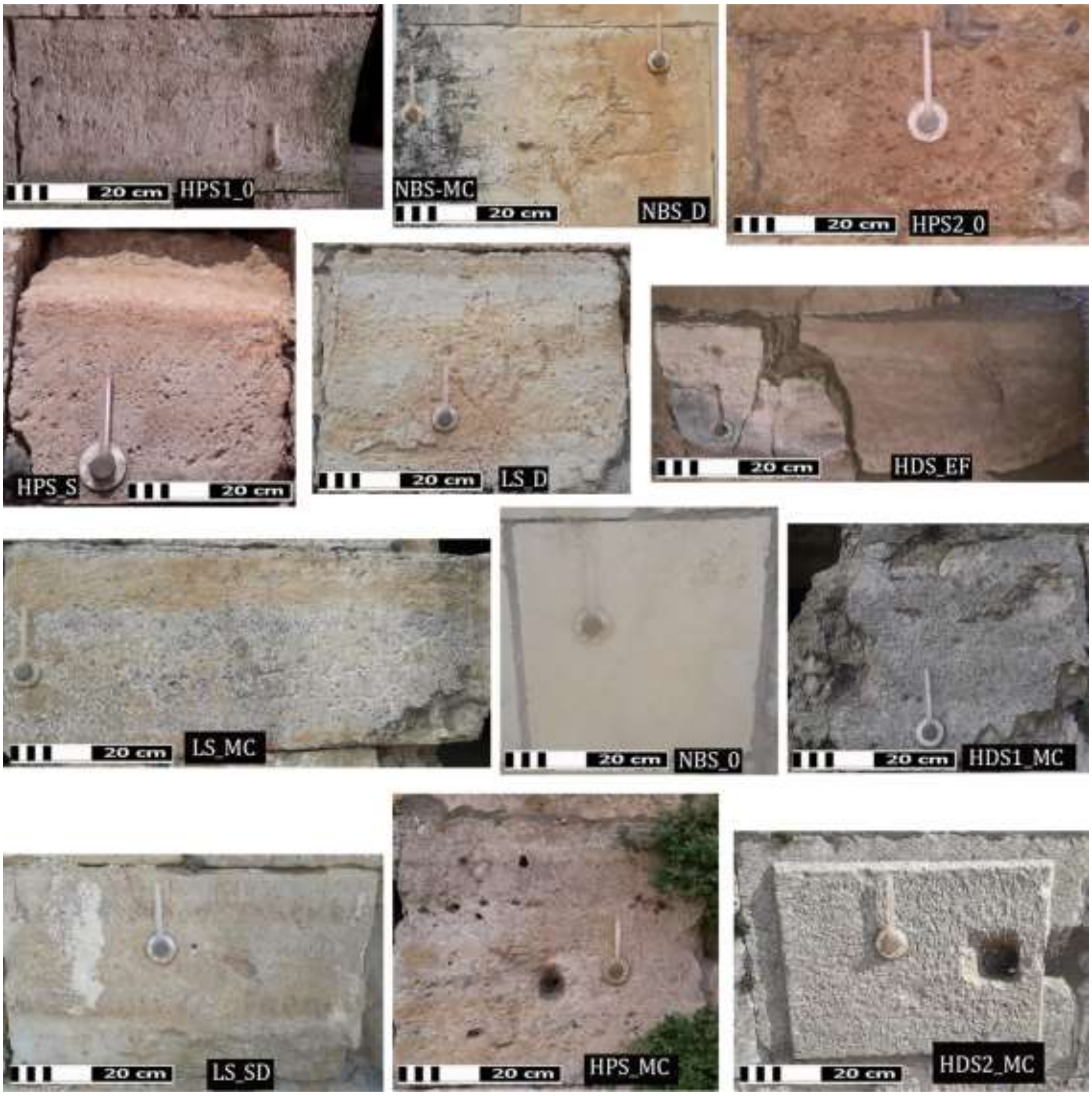

Figure 9 the tested stones by Rilem tube and Schmidt hammer.

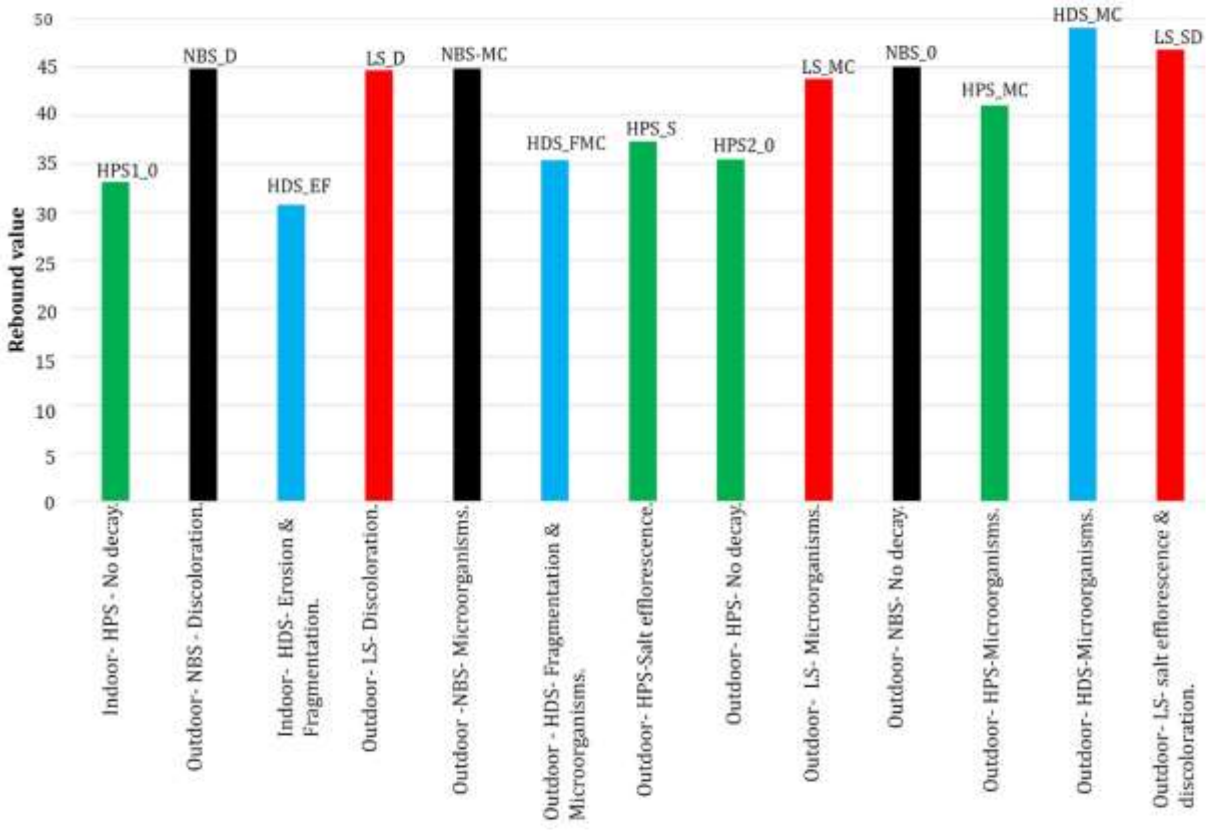

Figure 10 The average of the rebound values of the tested stones.

Among the tested stones, the three homogenous dense stones (HDS) with different decay types demonstrated different absorption behaviours and variety in their rebound values. HDS_EF was a very fragmented indoor stone with an eroded surface and cracks running the length of its height (Figure 9). This stone had a good absorption behaviour compared with two other tested homogenous dense stones (Figure 8). HDS_FMC was a stone in an external north façade of a building subjected to bombing shots. It had loss of material, fissures and fragmented parts, and its surface was colonised by microorganisms (Figure 9). This stone revealed moderated absorption rate, see Figure 8. On the other hand, the outdoor homogenous dense stone colonised by microorganisms (HDS_MC, Figure 9) did not absorb water (Figure 8). The rebound values of these HDS were different. The calculated compressive strength of HDS_FMC was 33.5 MPa, while for HDS_MC it was 88.7 MPa (Table 1). HDS_EF had the lowest rebound value and compressive strength (24.0 MPa) due to the fragmented and eroded surface. The rebound value of HDS_FMC was higher than HDS_EF and lower than HDS_MC (Figure 10). The mechanical shock due to

Table 1 The rebound values and the compressive strength of the tested stone.

Tested stone	Average of measured rebound values	Rebound value after correction	Calculated uniaxial compressive strength with eq. 1 (MPa)
HPS1_0	33.1	30.1	28.5
HPS2_0	35.5	32.6	33.7
HPS_S	37.3	34.5	38.3
HPS_MC	41.0	38.4	49.8
HDS_EF	30.7	27.6	24.0
HDS_FMC	35.4	32.5	33.5
HDS_MC	49.1	46.9	88.7
LS_D	44.7	42.2	64.8
LS_MC	43.8	41.3	60.8
LS_SD	46.8	44.4	75.3
NBS_D	44.9	42.5	65.8
NBS_0	45.1	42.7	66.7
NBS_MC	44.9	42.5	65.8

bombing most likely created micro-cracks and fissures on the stone surface, reducing the surface strength. The outdoor homogenous dense stone colonised with microorganisms (HDS_MC) had the highest rebound value in the homogenous dense stones group too (Figure 10). The tested homogenous dense stones which were colonised by microorganisms, had different absorption behaviour. When the microorganisms-colonised stone was exposed to mechanical shot, the absorption rate of the stone increased and its compressive strength decreased regardless of the presence of microorganisms.

The investigated laminated stones (LS) exhibited different absorption behaviour depending on their decay type, but their rebound values and compressive strength were close to each other. LS_D was an outdoor, laminated stone with discoloured surface and secondary pores (Figure 9). The stone revealed moderate absorption behaviour (Figure 8). LS_MC was an outdoor laminated stone colonised with microorganisms (Figure 9). The absorption rate leapt after the stone absorbed the first cubic centimetre of water from the tube (Figure 8). The last laminated stone (LS_SD) was an outdoor stone with discolouration and salt efflorescence on its surface (Figure 9). This stone did not absorb any water. The rebound values of all laminated stones were very similar; where the difference between the lowest and the highest value is 9%. The calculated compressive strengths of LS_D, LS_MC, and LS_SD were 64.8, 60.8, and 75.3 MPa; respectively (Table 1). The surface strength of the discoloured stone surfaces was slightly higher than the surface colonised with microorganisms (Figure 10).

The newly built stones (NBS) revealed different absorption behaviour but similar rebound values. NBS_MC and NBS_D (Figure 9) referred to one outdoor new built stone. It had a discolouration on the right side and thick microorganism colonisation on the left side of its surface. These different stone decays resulted in a big contrast in the absorption behaviour on the same stone. The discoloured part (NBS_D) had a higher absorption rate than the microorganism-colonised part (NBS_MC), where the presence of microorganisms modified the wettability property of the stone significantly. Even though the absorption trend of the (NBS_MC) was very low (corresponds to the first cubic centimetre of absorbed water) and then it increased, its absorption rate was still lower than the (NBS_D). Therefore, the type of deterioration was highly affecting the absorption behaviour of this stone. Like in HPS stones, the presence of microorganisms reduced the absorption rate of the stone. The compressive strength of the new built stones was around 66 MPa.

5. CONCLUSION

The field investigation and deterioration mapping revealed that the orientation and location of stone blocks influence the type of stone deterioration at the castle. The deterioration mapping of the external north and east façade of the same building revealed different decay types with various percentages. The most characteristic decay types of the east facade were the orange discoloration, colonization of microorganisms, salt efflorescence, and presence of higher plants; however, deposition of red-orange and grey microorganisms were the most dominated decay cases at the north façade. Both façades had grey microorganisms, higher plants, loss in stone material, and flaking parts in common but in different percentages.

The results of the Rilem tube test demonstrated that the absorption rate of the stone is highly dependent on the presence of a layer covering the stone surface. The stone with salt layer exhibited an absorption enhancement when the water pressure helped to dissolve the salt layer on the surface, facilitating the passage of water inward. That ability is most related to the thickness of the salt layer and the type of the salt itself. On the other hand, the stones covered by microorganisms showed relatively low to no-absorption behaviour where the layer of microorganisms highly affected the wettability property of the stone. In all lithotypes, the discolouration did not highly affect the absorption behaviour like the presence of salt or microorganisms.

The laminated stones had higher calculated uniaxial compressive strength values compared with the most of homogenous dense and porous stones. It is also well demonstrated that the rebound values of eroded surfaces and broken homogenous dense stones were low compared with non-damaged stones.

Even though its fragmentation, the homogenous dense stone had the same rebound value (calculated uniaxial compressive strength) as the non-weathered homogenous porous stones.

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Effect of consolidation on mechanical properties of oolitic limestone

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SUMMARY: The present study focuses on the mechanical changes that are caused by the consolidation of a highly porous Miocene limestone of Hungary. The studied lithotype was widely used as dimension and ornamental stone in monuments of Hungary from Roman times, but most intensively from the 19th century onward. It is a common practice; weathered stones are often treated with stone consolidants on-site during restoration works in order to strengthen the inner structure of stone and to provide better mechanical parameters. In the present study oolitic medium-grained limestone type from Sóskút (Hungary) was treated with ethyl-silicate (Remmers KSE 100) under laboratory conditions. Mechanical parameters such as compressive strength (UCS), modulus of elasticity (E), Poisson's ratio (ν) and indirect tensile strength (ITS) were measured on reference and consolidated samples. The uniaxial compressive strength and the indirect tensile strength has increased by nearly 60%, while the modulus of elasticity of ethyl-silicate consolidated porous limestone is nearly doubled due to consolidation. The lower changes were observed in Poisson's Ratio and dynamic modulus of elasticity. The results indicate that the consolidation leads to an increase in strength.

KEY-WORDS: porous limestone, consolidation, uniaxial compressive strength, Brazilian tensile strength, modulus of elasticity

1. INTRODUCTION

Consolidation of stones is a common practice in the remediation of heritage structures. This study aims to demonstrate the changes in mechanical properties after the consolidation of a porous Miocene limestone of Hungary. Emblematic Hungarian monuments of the 19^{th} century, such as the Hungarian Parliament Building, St. Stephan's Basilica and Citadella, were constructed from local limestone. These historic buildings display signs of weathering, and besides their visual appearance, the stone structures lost their strength (Török and Rozgonyi-2004). The limestone has high porosity (25-35 V%), low density, and low strength (Pápay et al. 2021). Ethyl silicate conservation agents are widely used to restore the strength of stone structures and provide better mechanical characteristics, especially for sandstone (Ludovico-Marques and Chastre-2014) and limestone (Pápay and Török 2010, Ban et al 2019, Pápay et al. 2021). For the evaluation of the efficacy of consolidation of the porous limestone, water transport properties, microscopic methods, colour measurements, porosity, pore size distribution, artificially weathering and mechanical parameters such as dynamic modulus of elasticity (E_{dyn}), drilling resistance and tensile strength (ITS) are used in the previous studies (Briffa and Vella-2019, Ferreira Pinto and Delgado Rodrigues-2008, Ksinopoulou et al.-2018, Pintér et al.-2008, Zornoza-Indart et al.-2016). Dynamic modulus of elasticity is a non-destructive method for assessing mechanical property because it is based on longitudinal and transversal ultrasonic pulse velocities (UPV). Uniaxial compressive strength (UCS) and static modulus of elasticity (E_{stat}) are rarely used in conservation science to evaluate the effect of consolidation. Dynamic modulus is higher than the static modulus of elasticity (Brotons et al.-2016, Fjaer-2019). Al-Shayea (2004) summarised formerly published values of both moduli of elasticity measured on different limestones. The dynamic modulus was measured in former studies in the order of up to 4-8 times higher, than the static modulus (Mashinsky-2003). This difference is caused by the magnitudes of frequencies and deformation during ultrasonic pulse velocity and uniaxial compressive tests, the heterogeneities and anisotropy of the investigated rock types (Davarpanah et al.-2020, Fei et al.-2016). Mockovciaková and Pandula (2003) studied the value of modulus of elasticities on different rock types (igneous, sedimentary and metamorphic rocks). They investigated that the difference between dynamic and static moduli are dependent on the rock type. Ultrasonic pulse velocity measurement is more sensitive to microcracks in the stone structure, while the results of uniaxial compressive strength testing method are affected by the visual inhomogeneities such as joints, veins and discontinuities (Mashinsky-2003).

The deterioration rate of the building stones in historical monuments has to be analysed with non-destructive technics. This is the reason why the dynamic modulus of elasticity is commonly presented in the literature (Graziani et al. 2015, Ksinopoulou et al. 2018, Ban et al. 2019). Tensile strength changes due to consolidation were also tested (Graziani et al. 2015), and even an over consolidation of limestone from Crete was observed (Maravelaki-Kalaitzaki et al. 2006). In some previous works, the increase in uniaxial compressive strength (UCS) of porous limestone was also measured (Columbu et al. 2017).

In this study uniaxial compressive strength, Young's modulus (dynamic and elastic), Poisson's ratio and indirect tensile strength of treated with KSE 100 and untreated oolitic medium-grained limestone from Sóskút (Hungary) were determined to assess the change in mechanical parameters due to consolidation.

2. MATERIALS AND METHODS

Porous limestone of Hungary presents a great variety in fabric characteristics (Rozgonyi 2002). Conservation treatment with KSE 100 was performed on a medium-grained limestone lithotype from Sóskút. It has millimetre-sized macropores and oolitic grainstone microfabric (Figure 1). The studied lithotype has average apparent porosity of 27V% and a bulk density of 1.68 g/cm3.

KSE 100 ready-to-use product by Remmers was used as stone consolidating material in the tests. KSE 100 stone strengthener is a compound of silicic acid ester. It has a low deposition rate (10%) and a density of 0.80 g/cm^3. Its active ingredient content is approx. 20% (KSE 100 Technical datasheet). Samples were treated in the laboratory under atmospheric pressure by full immersion in consolidant for 90 min.

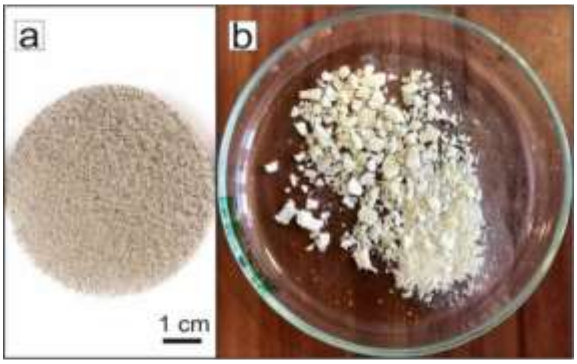

Figure 1 Medium-grained oolitic limestone (a) and the hardened consolidant Remmers KSE 100 (b)

The tensile strength was determined by indirect tensile test (ITS) on samples with a diameter/height proportion of 1/1 (diameter 54mm). In the course of ITS strength test, the specimen was loaded by parallel plates until fracture occurred by tensile stress along its diameter in the direction of the loading force (Figure 2). Displacement was measured parallel to the applied force with three displacement transducers 120°to each other. Calculation of tensile strength (σ_t) was performed with the Eq. 1 (Figure 2a).

$$\sigma_t = \frac{2F}{\pi \cdot d \cdot h} \qquad \text{Eq. 1}$$

where F was the applied force, d the diameter and h the height of the sample.

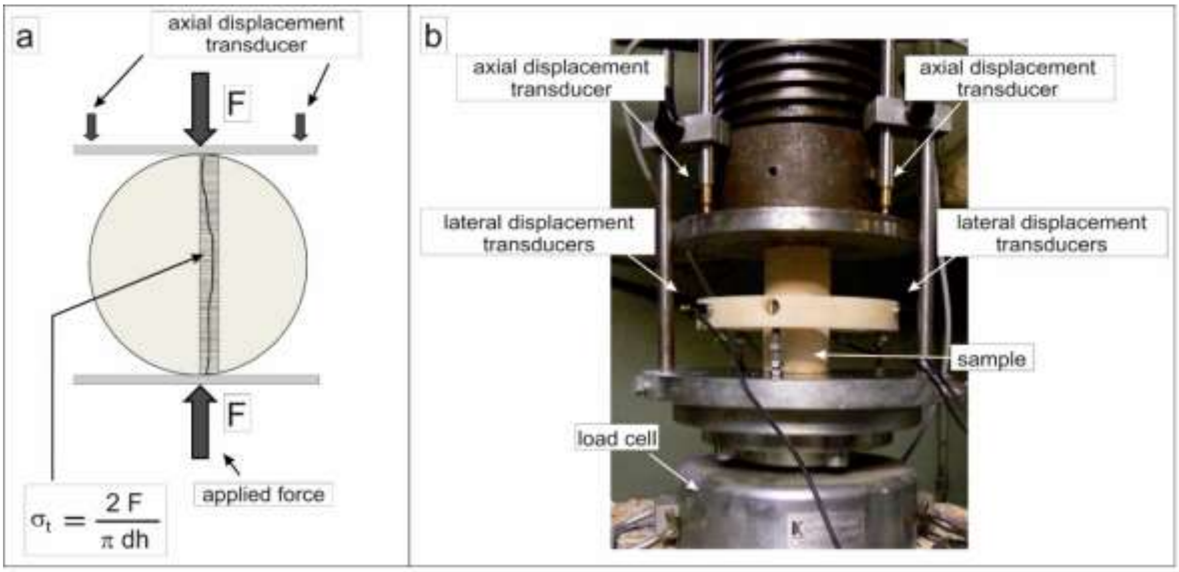

Figure 2 Determination of tensile (a) and uniaxial compressive strength (b)

Uniaxial compressive strength (σ_c) was determined on samples with a diameter/height ratio of 1/2 (diameter 54mm) with measuring the displacements parallel and perpendicular to the applied force with axial and lateral displacement transducers, respectively (Figure 2). Displacement values were calculated from the average of the data of 3 transducers placed in 120° from each other. Static elastic modulus (E_{stat}) and Poisson's ratio (ϑ_{stat}) were determined from the linear (elastic) section of the uniaxial compressive stress (σ_{ax}) – axial strain (ε_{ax}) curves and from the linear section of the axial strain (ε_{ax}) - lateral strain (ε_{lat}) curves according to the equations Eq. 2 and Eq. 3, respectively.

$$E_{stat} = \frac{\Delta\sigma_{ax}}{\Delta\varepsilon_{ax}} \qquad \text{Eq. 2}$$

$$\vartheta_{stat} = \frac{\Delta\epsilon_{lat}}{\Delta\varepsilon_{ax}} \qquad \text{Eq. 3}$$

Dynamic elastic modulus (E_{dyn}) have been determined with the help of the following two methods:

i) Ultrasonic pulse propagation time of longitudinal and transversal wave was determined with UP-SW transducers (Frequency of 80 kHz) without coupling material (Geotron UKS 12 equipment, LightHouse 2000 software). After measuring the propagation velocity of the longitudinal wave (v_p) and the transversal wave (v_s) through cylindrical samples the dynamic elastic modulus (E_{dyn}) and Poisson's ratio (ν_{dyn}) were calculated using Eq. 4 and Eq. 5.

$$E_{dyn} = \rho_{bulk}\, v_p^2 \frac{(1-2\vartheta_{dyn})(1+\vartheta_{dyn})}{(1-\vartheta_{dyn})} \qquad \text{Eq. 4}$$

$$\vartheta_{dyn} = \frac{v_s^2-0.5v_p^2}{v_s^2-v_p^2} \qquad \text{Eq. 5}$$

Transversal wave velocity results are only available for the reference samples.

ii) E_{dyn} was calculated with the simplified equation Eq. 6 from the longitudinal ultrasonic wave velocity (v_p) and bulk density (ρ_{bulk}) of reference and consolidated samples. The ultrasonic pulse propagation time of the longitudinal wave was determined on cylindrical samples with a diameter of 54mm and height of 54mm, with Geotron UKS 12 equipment (transducers UPG 250 and UPE). A very thin layer of coupling agent was placed between the stone surface and the transducers during the measurement. The velocity of the longitudinal wave (v_p) was obtained from calculations with LightHouse 2000 software.

$$E_{dyn} = {v_p}^2 \cdot \rho_{bulk} \qquad \text{Eq. 6}$$

3. RESULTS AND DISCUSSION

The open pores spaces were reduced after consolidation, leading to a weight increase. The weight changes of consolidated samples were measured in time showing a clear trend (Table 1). Immediately after the consolidation weight increases of 9.4 to 12.4% were recorded, however after 90 days only 1.5 and 1.9 w/w% KSE 100 were found in the pores of the limestone specimens (Table 1).

Table 1. Weight changes in time after consolidation (w/w%)

sample	after consolidantion	21 days	90 days
UCS (No. 216)	11.9	2.9	1.9
ITS (No. 104)	12.4	3.0	1.9
ITS (No. 113)	9.4	2.5	1.5

The results show that both the uniaxial compressive strength and the indirect tensile strength increased significantly after the treatment with tetraethyl silicate. The stress-strain curves of consolidated and non consolidated limestone samples during uniaxial compressive loading mark the mechanical changes linked to consolidation (Figure 3). Due to the treatment with tetraethyl silicate the slope of the stress-strain curves increased at the same time as the deformability decreased (Figure 3 green arrow). As a consequence, the static modulus of elasticity increased and the Poisson ratio decreased after consolidation.

The typical stress-strain diagrams of limestone treated with KSE 100 and reference specimens during indirect tensile strength test are illustrated in Figure 4, where the x-axis shows the strain parallel to the applied force and the y axis displays the indirect tensile stress. The decrease of deformability and the increase of stiffness is not observable during indirect tensile loading. The deformation behaviour of the consolidated samples is different, but the strength increase is clear.

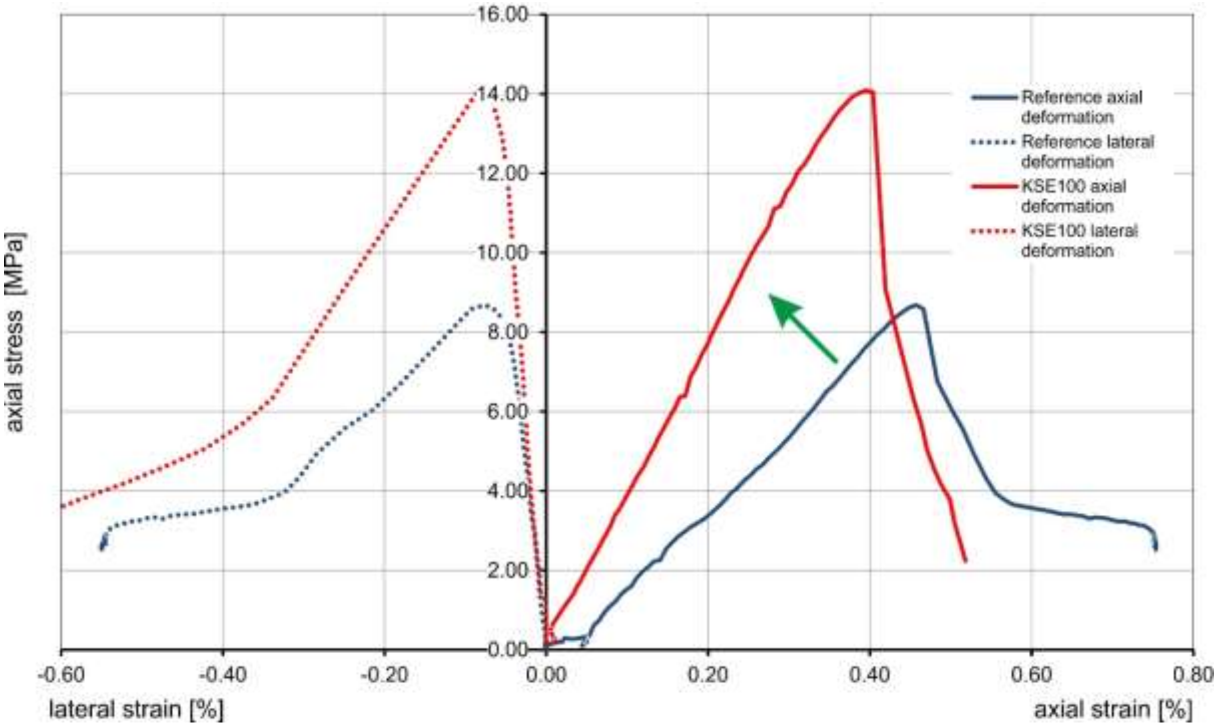

Figure 3 Typical stress-strain curves of reference and consolidated porous limestone in UCS test (green arrow shows the changes)

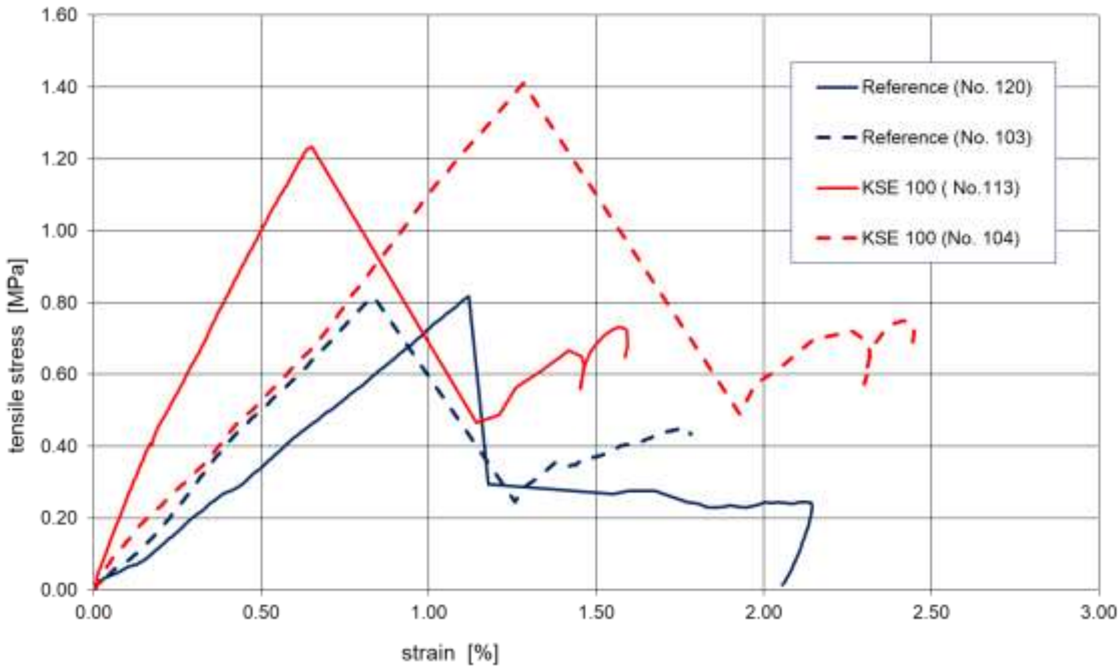

Figure 4 Stress-strain curves of reference and consolidated porous limestone in ITS test

The average strength values of UCS and ITS testes are summarized in Figure 5a and Table 2. Consolidation with ethyl silicate caused a significant change in the strength parameters (Figure 6). An increase in compressive strength (+62%), static modulus of elasticity (+81%), dynamic modulus of elasticity (+35%)

and tensile strength (+61%) were measured. To the contrary, the Poisson ratio decreased after consolidation with 17%. The improvement in tensile strength of Miocene limestone from Sóskút is much lower than the value detected in Globigerina Limestone (+126 %; Graziani et al. 2015), but higher than the results of Giallo Terra di Siena (32 %; Graziani et al. 2015) and St. Margarethen Limestone (+42 %; Ban et al. 2019). The former reported growths in dynamic modulus of elasticity such as + 56 % for Globigerina Limestone, + 63 % for Giallo Terra di Siena (Graziani et al. 2015) and 97 % for St. Margarethen Limestone (Ban et al. 2019) are 2-3 times higher than our result (35%). Ksinopoulou et al. 2018 showed a lowerchange (+13.5 %) in E_{dyn} of Rethymnon porous limestone.

The minor differences in dynamic modulus of elasticity calculated from Eq. 4 and Eq. 6 are given in Table 2. The ratio between the dynamic and static modulus of elasticity referring to the reference stone was 4.9. This ratio is very high compared to former data, where this ratio is between 0.85 and 1.86 (Al-Shayeda 2004). This significant difference between the results can be attributed to the much higher porosity of the investigated stone type in our study. Sedimentary rocks also had a wide range in the ratio between dynamic and static modulus of elasticities (Mockovciaková and Pandula 2003). In their study, the ratio was for sandstones almost one (1.02) and for dolomite very high (2.8). This phenomenon supports the theory that macropores, grain size, porosity and micro-cracks increase the difference between the static and dynamic elasticity constants such as modulus of elasticity and Poisson ratio (Davarpanah et al. 2020). It has to be noted that the stone type in our investigation is very heterogeneous due to its high porosity (27 V%), low bulk density (1.68 g/cm^3) and the presence of macropores. The deposition of the silica gel in the pores causes the improvement of physical parameters and a decrease in the difference between the two moduli of elasticity (from 4.9 to 3.66, Figure 5b). In the present study, the ratio between the dynamic and static Poisson ratio was for non-consolidated oolithic limestone nearly one (1.1) thus, the dynamic Poisson ratio is higher than the static one. Our finding is similar to Fei et al. (2016) and Davarpanah et al. (2020).

Table 2 Strength (UCS and ITS), static and dynamic modulus of elasticity, static and dynamic Poisson ratio of reference and with KSE 100 consolidated porous limestone

	UCS [MPa]	static modulus of elasticity [MPa] Eq. 2	dynamic modulus of elasticity [MPa] Eq. 4	dynamic modulus of elasticity [MPa] Eq. 6	static Poission ratio [-] Eq. 3	dynamic Poission ratio [-] Eq. 5	ITS [MPa] Eq. 1
reference	8.68	2166	10513	10589	0.18	0.20	0.82
KSE 100	14.08	3912	-	14336	0.15	-	1.32

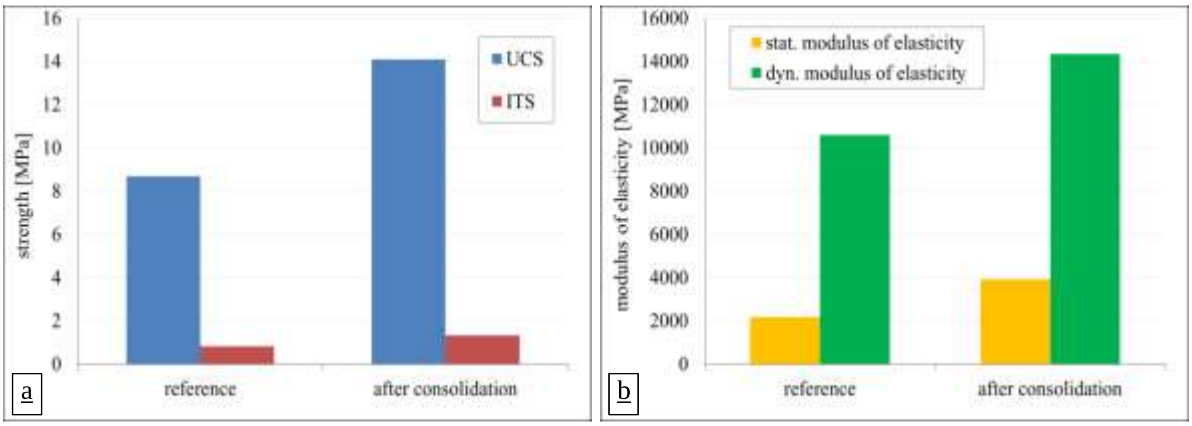

Figure 5 Strength (UCS and ITS) of reference and with KSE 100 consolidated porous limestone (a); static and dynamic modulus of elasticity of reference and with KSE 100 consolidated porous limestone (b)

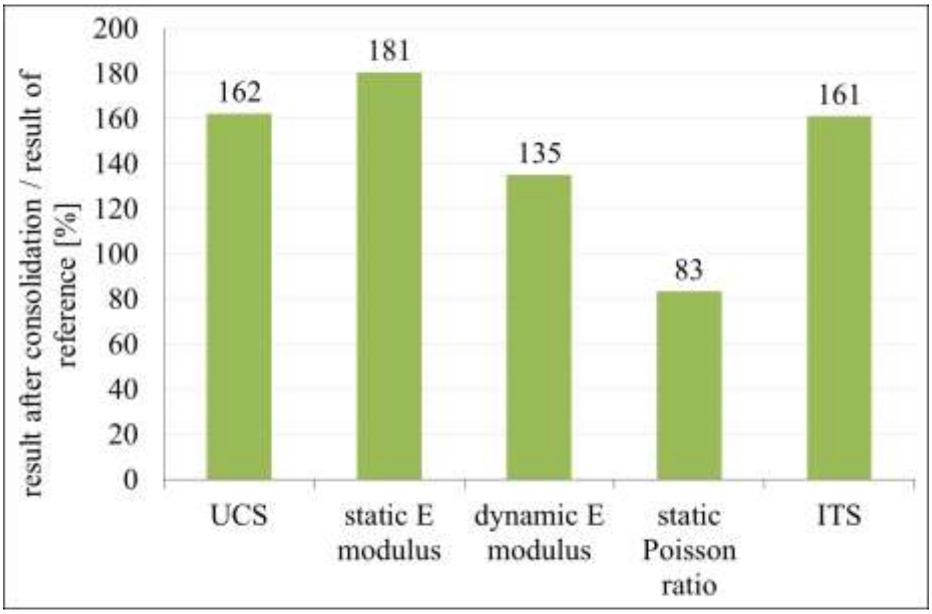

Figure 6 Change in UCS, static modulus of elasticity, dynamic modulus of elasticity, static Poisson ratio and ITS after consolidation

4. CONCLUSIONS

Miocene medium-grained porous limestone from Hungary was treated with the silicic acid ester (KSE 100) consolidant to evaluate changes in mechanical parameters due to consolidation.

Our study indicates that the performance of consolidation with KSE 100 on porous limestone causes a significant increase in mechanical parameter such as uniaxial and tensile strength and modulus of elasticity. Opposite to the strength increase, the deformability of the porous limestone decreased, and the rigidity increased due to consolidation.

The change between the dynamic and static modulus of elasticity after consolidation was much greater than the results reported in literature. An explanation for this phenomenon is the very weak structure of the investigated lithotype with its high porosity, very low bulk density and the presence of macropores. The deposition of KSE 100 in the pores caused a reduction in the Poisson ratio.

The results indicate that the consolidation leads to an increase in strength. However, the increase in strength alone does not justify the use of consolidant since other properties such as deformability, porosity or water absorption are also critical parameters when the justification of such intervention is judged.

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Development, validation and selection of consolidation treatments require specific and distinct approaches

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SUMMARY: The study of consolidation treatments is carried out under distinct contexts and perspectives that aim to achieve different objectives; therefore, it is logical that several working methodologies and reporting styles may exist. The development of a new product or a new treatment protocol should aim to prove its effectiveness and define, in general terms, its domain of applicability. Issuing advice on direct practical applicability is not necessarily positive at this stage and advancing with premature conclusions can be unwise. The validation of research data is a fundamental step before practical implementation is considered. It is relevant to identify the specific situations in which the product or process is applied and to define the methods and identify the conditions that allow to guarantee their applicability. This is the ideal stage for all knowledge to be subjected to scrutiny by the scientific and technical community. The selection of a consolidation treatment to solve a practical problem must be approached as a bottom-up approach, in which the type and properties of the stone, the deterioration patterns and the cultural values of the object must be taken as a master guide. The consolidating product and treatment protocols are selected to solve each concrete problem, where ambiguity and general considerations can add more harm than good.

KEY-WORDS: stone consolidation; selection methodologies; selecting consolidation treatments; decision making

1. INTRODUCTION

The consolidation of deteriorated stones is the most researched topic and certainly the one with most published references in stone conservation. And yet, this wealth of research information has not had a parallel impact on improving conservation practice, with many practitioners still following overly simple decision-making approaches or directly resorting to supposedly proven recipes. There is no simple explanation for this divergence between scientific results and its practical application, and there is certainly no reason to blame anyone responsible for this situation. Not everything will have been done incorrectly, but certainly many things could have been done more effectively.

As discussed in another communication to this symposium (Delgado Rodrigues and Charola 2021), the transfer of knowledge between scientists and professionals is of paramount importance, as long as it integrates the appropriate models and a clear understanding of the needs and restrictions of the practice, and uses language and communication channels directed to these professionals.

When stone consolidation is considered, every effort must be made and precautions taken to convey accurate and reliable information, as gaps, inaccuracies, or maladjustments can result in negative consequences for the last recipient, the cultural object being restored.

As in any other field of research, following professional ethical rules is mandatory and adopting best practices and respecting the confrontation between peers are common sense measures for success. Furthermore, in order to reach conservation practitioners, here typified as conservator-restorers and conservation-scientists, some details seem to need a better conceptualisation and an improved way to transmit the results of the research.

A central idea of this article is the need to have the objective of the scientific message clearly and objectively identified and properly transmitted. Of course, this can happen naturally as a corollary of proper research planning aimed specifically at responding to the headlines highlighted here - *developing, validating and selecting consolidation treatments* - but most of the time the information comes from multipurpose projects, where the need for clarification presupposes even greater relevance. It is, therefore, important that the context of the research and the purpose of the communication are clearly stated.

The development of a new consolidation product is the first phase in a research chain that may eventually lead to a new approach in the practice of conservation, but being a first step, it is neither expected nor advisable that its immediate result are guidelines directly applicable in practice. Of great importance is the information on all relevant details that may allow the peer researchers to proceed to the second major stage of this process, which will be the validation of the results.

This validation phase can start with the original developers of the product, but it is completed only when the peer researchers consider it as their own research material. This must be clearly assumed by the developers as an essential step and all collaboration must be offered by them so that the validation exercises are as complete and accurate as possible. A product considered promising by the developer and without peer validation is most likely doomed to failure and will not go beyond the beakers and test specimens of its creator.

The selection of a consolidation treatment is the final and most challenging step in this chain. Considering that the first two phases can be classified as top-down approaches, in the sense that they start from the product and descend to find the respective implications, the selection of a treatment must be taken as a typical bottom-up approach. The choice of the appropriate treatment is highly dependent on the context, namely the stone material and its deterioration patterns, the significance of the object, the prospects for its future use, as well as the technological and professional resources available.

The terms consolidation product and consolidation treatment are understood here as different concepts and, for the sake of clarity, they should be used unambiguously. The concept of "consolidation treatment" encompasses a consolidation product, the conditions used to apply it and the circumstances prevailing at the time of application. A product is described and characterised through its chemical and physical properties, while a treatment requires information on what the product is, its concentration, solvent used, etc., plus the application protocol and the amount applied, and its understanding gets complete only when information is given on the conditions of the surface where it was applied, the environmental conditions prevailing at the time, and the overall curing conditions. Information about the product, the application protocol and the amount applied are the minimum essential information requirements of a consolidation treatment.

For developing the perspective here advanced, the article will follow these three major phases: development, validation, and selection.

2. A THREE-STAGE MODEL OF RESEARCH IN STONE CONSOLIDATION

To enter the field of conservation research, mental curiosity and a propensity for research are necessary personal attributes, while the choice of research topics, the resources available, and the research environment are typically contingent circumstances. While some have the opportunity of freely choosing the research argument and work within wide time frames, usually when in the academic domain, others are required to work on narrow topics to achieve concrete goals within limited time frames. Both are relevant types of research activity, but their outputs have distinct purposes and therefore should be assessed and valued with distinct criteria.

Research to understand the interaction of a product and a particular stone, or to study the chemical evolution of a product under natural or artificial aging, are examples of topics that can be studied from both perspectives, but while the academic world is satisfied with a solid and profound methodology and clear and justified results, whatever they may be, an adequate explanation to help make a decision is probably needed from the other perspective.

The “distance” that a given study is from a practical decision defines its “academic” or “applied” character, and it is recommended that the actors consider their production under a parallel framework. An academic work must be evaluated for its original scientific content, while its practical applicability is a secondary evaluation criterion. An applied study must be evaluated for its contribution to solving a practical problem, while the scientific arguments used (which for the most part are probably not original) are to be taken as support tools and comfort measures to accept the conservation solution.

Because of their broad scope and freedom of choice, academic studies are impossible (and therefore not desirable) to classify into categories and are thus left out of the following considerations. That said, it is hoped that such studies will not fall into the temptation to point out “practical” solutions based on generic considerations whenever critical points of concrete situations have not been researched.

Professionals on stone consolidation are supposed to be familiar with the best scientific information available, but it is unrealistic to assume that they could dig through the endless information sources with potential impact on the problem at hand. This article is aimed at all those who wish and deserve to be a closer source of information and who are prepared to organize their research and make information available, considering these professionals as target users.

A consolidation solution for a deteriorated stone case must be based on adequate knowledge of the situation in question and on the integration of information that helps to design a convenient consolidation treatment. The identification and proper characterisation of the situation are of paramount importance here, but the approaches to achieve them are outside the scope of this article. Therefore, the focus of the next sections will be on the potential consolidation products and all the information that can help shape them into an appropriate consolidation treatment.

2.1 Development of consolidation products

Most of the consolidation products currently in use were discovered and started to be used years ago, and new products are not likely to appear on the market anytime soon in significant numbers. However, small or large improvements are being made to existing products, and any new changes must be considered as if they were a “new” product.

Any “new” product or any modification of existing ones acquires a specific objective of great significance and it would be desirable that its inventors and promoters adopt a proactive attitude in obtaining and disseminating relevant and accurate information to the potential users of their products.

There is no maximum limit to the depth and extent of the information to be offered, but there will certainly be a minimum of information to be provided and an appropriate way to transmit it.

In principle, a minimum information must be provided on the following characteristics, as applicable:

- i) Chemical composition and structural information, catalysts, and any other complementary compound,
- ii) Relevant physical characteristics, such as viscosity, density, etc.
- iii) Indication of the specific and adequate solvents, target range of concentration values to be used.

A first insight into the product action should be indicated, namely:

- iv) The acting mechanism, whether it is a consolidant, or a consolidant and water repellent combined,
- v) The expected interaction with the stone material, for instance, the type of coating, whether it is film-forming or void-filling, the adherence bonding to material, etc.
- vi) The target materials where it is to be used,
- vii) Any health and safety issues applicable.

Some fundamental physical properties of the treated stones are difficult to obtain under totally satisfactory test conditions, and “validation” and “selection” studies often avoid them or work with insufficiently representative conditions. Thermal expansion coefficient, Young's modulus and water expansion are essential to interpret long-term performance, but reliable values are rarely found in the literature. These properties must be determined in large and homogeneous samples, but, with most consolidants, only a consolidation under vacuum will allow to obtain a homogeneous and complete impregnation. Therefore, it would be highly beneficial to have developers and promoters carrying out these demanding experiments with selected types of stones to obtain some benchmarking results that would serve as a guide for potential users. Benchmarking situations could include two or three situations per lithotype identified as being a realistic target for the “new” product.

Besides the above-mentioned minimal information, these properties on benchmarking stone samples are recommended to be included in the “Product Information Sheet”. This is the information needed to form a first opinion on a stone consolidant, regardless of the specific situation in which it will be used.

Any new product or modification of the existing one must be validated by the community of peers and, therefore, it is essential that the product is available to other researchers and users at reasonable costs or that precise indications are provided to prepare it at home.

Obviously, some first validation steps can be carried out at this stage, but authors should refrain from offering very specific indications for using their product before obtaining additional peer validation.

2.2 Validation of consolidation products and treatments

Most of the published literature can be grouped under a generic title of “validation” studies. In fact, many articles contain information that can be integrated into a validation operation, but those that are explicitly designed to perform validation of specific properties are scarcer.

Many articles are based on a broad scope plan where the phases and objectives have as their main motivation the production of scientific knowledge and, therefore, it is not always simple to decipher them in terms of what can be extracted to advance the conservation practice. As stated before, this is not necessarily a shortcoming, but it may constitute a real difficulty for professionals who are looking for a solution to their specific problem of stone deterioration.

For researchers specifically interested in the validation of conservation actions and who wish to have an impact on the conservation practice, it is advisable to keep in mind who the recipients are and what may be of direct interest to them. To achieve this goal, information within this category must take into consideration the following main topics:

i) Clearly identify the actions or properties under validation,
ii) Use work processes and interpretation algorithms as simple as possible,
iii) Offer clear conclusions and provide thorough explanations,
iv) Make explicit what are the validity limits of the conclusions.

One important point, which we can call the "scale factors", is rarely considered, even in properly prepared validation trials. For instance, depth of impregnation is frequently taken into account in "validation" trials, but it is very rarely indicated whether other depths can be reached and how the process of reaching them can be mastered.

As stated before, the application protocol is an important component of a consolidation treatment and it should be clear how the information from laboratory studies can be translated into practice. The amount of product applied per unit area is one of the few precise indications that can be used to scale the results of the laboratory to the practical world. Concrete indications that can help to reach different depths of impregnation, such as the use of other solvents or other concentrations, are valuable complementary information.

No individual validation exercise can assume a generic range of applicability and, most likely, no laboratory application fully represents the real situations that need consolidation. Geometric samples are essential for making accurate measurements in the laboratory, but most methods used to monitor the consolidation action are not applicable on site. The conclusions drawn from the data thus obtained and any recommendations based on them should take into account how users will implement and control them.

Usually, laboratory research studies use samples from a quarry, or at most, samples subjected to artificial aging. None of them is a faithful representative of the real situations of deteriorated stones. Deteriorated areas are very fragile situations and consolidation is always a very risky conservation action, known for frequently having serious negative impacts. The "validation" studies, especially those that intend to offer recommendations applicable in practice, should keep in mind that most of the failures occur due to risks of excessive incompatibility and not due to insufficient strengthening capacity (Fig. 1).

Figure 1 – A thin superficial indurated crust, possibly caused by a past consolidation treatment, often ends up failing by excessive incompatibility with the substrate, as happened in this very porous limestone

When preparing this type of research studies, it is important to keep in mind how the end users of their results will translate them into operational information. Most likely, they have a different stone to work with, so it is important to make it clear what the validity limits of your conclusions are and how they can be extrapolated. To what types of stones are these conclusions applicable? What is the porosity range encompassed in this validation? Can the results be extrapolated to other porosities? And for other types of stones? And so forth.

2.3 Selection of consolidation treatments

Selecting a consolidation treatment to solve real problems of deteriorated stones is never a simple operation and there are no recipes to identify the right solution and guarantee a totally satisfactory result. It is a job to be pursued as a team, where the conservation-scientist and the conservator-restorer play the main roles. Any specifications introduced in the tender documents will never be able to adequately predict all the small details of the concrete situations, and it is advisable to leave room for adjustments and improvements when the chosen contractor undertakes the work.

In rare specific situations, comprehensive studies aimed to characterise the situation in question and to identify and validate the consolidation solution are carried out, but in most cases, this is not possible, and the selection has to resort to much more modest means.

The identification of the stone material and the description of the deterioration patterns require some knowledge, but both can be reasonably achieved by competent conservator-restorers and conservation scientists on the workshop premises with minimal technical resources. There may be other occurrences of relevant implications, such as the presence of salts or previous treatments, which may imply additional studies and require additional technical or specialised assistance for its satisfactory understanding.

An adequate understanding of the situation under analysis is the basis for selecting the consolidation treatment and some decisive options are taken based on it. For example, heavily damaged delicate areas will not withstand high mechanical imbalances and, therefore, high-strength consolidants can reasonably be discarded for such uses. Instead, low porosity cracked stones, such as granites, can have very stable surfaces where a consolidation reinforcement up to the substrate strength level can be accepted.

The next steps of the decision-making process rely on each other's experience and should seek support from the available literature, but it has to be admitted that not all professionals are prepared to carry out extensive literature searches to extract the information that will help them find the most appropriate solution for their specific problem. Furthermore, the potentially decisive clues are scattered among a confusing amount of uninteresting or inapplicable information to the point that users become unmotivated and take refuge in their experience or in a more or less specific and meaningful someone's suggestion or advice.

The collection of relevant information takes time and implies some investment and it would be valuable to have the end users and information providers tuned in converging processes so that the paths taken for the search and integration of information fit the models used for research and validation of consolidation treatments. Some tips to help in this convergence are presented below.

The chemical and mineralogical composition of the stone is the first key to search, and the type of voids it has (pores of equidimensional shape versus fissures or cracks) is the next. Total porosity helps to restrict searchable targets inside each identified cluster. Look for information on sandstones, if your material has a similar composition, or on limestones likewise. Within each group, compare the information for porosity ranges that do not differ more than a few percent values from yours; limestone or sandstone of low porosity and high porosity cannot be compared and the results can be totally non-transferable to each other.

Granites and other igneous rocks share a similar silicate composition with sandstones, but their fissure-type voids give them a totally distinct behaviour vis-a-vis the consolidation performance; a similar reasoning can be applied to marbles and limestones. More detailed guidelines can be found elsewhere (Delgado Rodrigues 2021).

The amount of information applicable to each one's problem is thus significantly reduced using these three key elements: the chemical composition of the stone, the voids morphology, and total porosity. A final and decisive element of narrowing comes into play when the current deterioration pattern, the decay profile, and the meaning of the object are taken into account.

Very likely, this last narrowing procedure will end up without any entirely applicable information source, which will require that other reasoning processes be called to help. Delicate surfaces, with deteriorated areas loosely adhering to the substrate, can accept only very light consolidation actions and, therefore, the search for information should favour the softest strengthening products and the most controllable treatment protocols. Having validation studies explicitly addressing such issues would be a relevant benefit for professionals.

The treatment of much deteriorated areas may imply the inevitable loss of the loosest detaching particles, but an appropriate scale-up approach (Delgado Rodrigues and Ferreira Pinto 2019) can help find a scalable treatment, or sequence of treatments, to minimise losses and achieve the minimum strengthening needs (Fig. 2).

Figure 2 – Consolidation of a delicate surface showing strong signs of deterioration requires a slight increase in strength and with a very low degree of incompatibility. High-strength increments and very shallow impregnation depths, as this photo suggests, can compromise the entire surface in the medium to long term

For mastering the consolidation action, the conservator-restorers have some variables with which they can work, namely, the type of product, its concentration and the type of solvent, the application protocol and the quantity to be applied. The conservator-restorer must be familiar with how to work with these variables and, likewise, it would also be desirable for validation studies to consider these issues as their validation targets.

An important and often overwhelming barrier that professionals encounter when trying to use the literature data in defining the treatment to be adopted comes from the difficulty of transposing the results obtained in samples of sound stone, of regular surfaces, treated under controlled laboratory conditions, for the conditions of deteriorated surfaces. Some experience and great care must be taken in such extrapolations and no concrete guidelines can be offered. Just as a broad guidance, it can be considered that any conclusions that these studies offer on the strengthening effect can be taken as the maximum that can be achieved onsite for similar treatment conditions, while all the harmful or incompatible results reported should be considered as the lowest level of harmfulness, which is likely to be worst in the real world (Fig. 3).

Figure 3 – Sound surfaces should not be consolidated as strength reinforcement is not logically justified, its presence is not innocuous and can compromise the long-term performance due to excessive incompatibility

3. DISCUSSION

In 1977, the National Bureau of Standards (USA) produced an important report on stone consolidants, under the generic designation of stone preservatives, where over 50 of the most common products available at that time were tested (Sleater 1977). The work was based on realistic perspectives of what stone consolidation means and followed an intelligent experimental approach to seek answers to the difficult task of selecting which stone consolidant to use.

Despite the interesting information it contains, this report was eventually known and mainly cited due one of its main conclusions: "*None of the stone preservative materials evaluated fulfilled all the proposed performance criteria*." Today, this sounds like a truism that does not do justice to the work reported there. Of much greater relevance is the prospect that the selection of consolidants must be supported by criteria based on experimental evidence. The 15 criteria taken into account show how complex the task is, which, even so, is not fully defined, because, as it is written there, "*The user must therefore decide which performance requirements for stone preservatives fit his problem of stone decay, and which criteria should be applied in selecting preservatives*" (Sleater 1977). This is a fully updated statement that highlights that at the very beginning of the selection process is the "*problem of stone decay*", for which specific "*performance requirements*" are to be identified, to complete with the confrontation of the potential consolidant against the proper screening criteria.

The citation of that "dramatic" conclusion by subsequent authors (v.g. (Clifton 1980), (Clifton and Frohnsdorff 1982), (Price 1982), (Doehne and Price 2010)) shows how attractive a "one-fits-all" solution would be, although all of them were aware that "*it is almost certain that no product could be found that would meet all the criteria*" (Price 1982).

Great efforts were made to assist decision makers in selecting the appropriate consolidant and there was a belief that a procedure to assist in this selection was considered achievable. In 2001, ASTM issued a Standard Guide for Selection and Use of Stone Consolidants (ASTM-E2167-01 2008) that was subsequently reapproved in 2008 and withdrawn in 2017. Despite the helpful guidelines it contains, the document was more of a checklist than a standard, and it was far from being a clear help to anyone who has a serious consolidation problem to resolve and has to decide which consolidation treatment to apply. It did not overcome the need for a personal appreciation of the problem with its inevitable subjectivity, and it can be questioned whether the inconvenience of having a standard that cannot be applied "by the book" was one of the reasons for withdrawing it.

The fate of this standard is informative about the trends that have permeated the field of conservation science. The continuing search for reliable testing tools and methods, the realization that the decision on how to select a consolidation treatment is difficult and often overwhelming, and the harsh reality of recognizing that professionals in charge of deciding how to resolve a deteriorated stone problem must always include subjective evaluations with an inescapable increase in responsibility.

The test is the quintessence of conservation science and there is no limit to the type, number and depth of tests that can be applied to the study of stone consolidation. A known set of tests primarily intended to testing stone was proposed by RILEM (RILEM-25PEM 1980), and a comprehensive review on testing methods and criteria for the selection/evaluation of products was published elsewhere (Laurenzi Tabasso and Simon 2006); the CEN/TC346 group is currently producing standards and guidelines under this same theme.

Therefore, the problem is not insufficient testing capacity, but how to evaluate the test results. This is not a recent problem, showing that it remains an unsolved issue. Answering questions such as what these results are useful for or what to do with what, in general, are good starting points, and it would be beneficial to have authors always in tune with these basic purposes.

In the article cited above (Sleater 1977), the author showed that a test result must be framed with a criterion to verify compliance with a performance requirement. Aware of the multiplicity of tests and of the lack of straightforward evaluation procedures, Price (1982) grouped the evaluation techniques into categories, defined by the broad domain they have in common: "*tests primarily for untreated stone*" and "*tests specifically for treated stone*", namely for "*characterisation of treatment*", and "*tests for assessing how well treatments meet objectives*". A few years later, with an increasing abundance of tests and experimental results, and given the prevailing confusion as to what all this information means and how it can be put at the service of stone conservation, (Sasse and Snethlage 1996) reworked the testing purposes and put forward six categories that illustrate the wide diversity of research interests: i) *Basic tests*; ii) *Adjustment tests*; iii) *Application tests*; iv) *Identity tests*; v) *Production control*; vi) *Long-term assessment tests*.

In general, research projects and published information do not explicitly identify where, in the chain that leads to solving practical conservation problems, their objective lies, and this fact creates additional difficulties for professionals who wish to be updated with the available scientific information. The division into three categories here advanced, "development - validation - selection", is simple enough to be adopted by researchers and would be of great value to help professionals navigate the multiple dimensions of the published literature: "stones-products-conservation-theoretical-practical-academic-applied studies".

The "selection" category should be reserved for those studies that are directly involved in solving a practical consolidation problem. It is a type of applied study whose result will be directly integrated into the decision process that leads to adopting a specific solution to a concrete problem of deteriorated stone. The characterization of the deteriorated stone, any on-site and laboratory tests designed to answer specific questions of the problem in question can be included in this category. Studies of this type, designated as "case studies", have a somewhat pejorative connotation and are therefore underestimated in scientific publications, a regrettable situation that sends these potentially informative practical studies to the shelves of laboratories and condemns them to public oblivion.

Knowing the arguments and reasoning behind the adoption of a consolidation treatment can be as beneficial for the progress of stone conservation as a high-quality academic study. Of course, not all case studies are interesting, but even poorly solved cases may serve as benchmarking for defining the thresholds of unacceptable quality. For instance, deciding that the consolidation of very important objects in a specific archaeological site made of limestone was to be carried out with "*The water repellent product ethyl silicate, …*" because it is " *… superior to other synthetic polymers (applied in conservation)* …" and "… *preserves water wet ability of such treated stones … can be used to reduction of salts*", without any characterisation of the properties of the stone and without any concrete evidence of how such a treatment would behave is an approach absolutely to be avoided [*reference discarded to avoid embarrassment*]. In any case, this can be used as a good example of what should not be done.

"Validation" is a broad category that includes the studies on stone consolidation that have no immediate link to a decision-making process aimed at solving a problem of deterioration of stone in concrete. The preparation of theses and funded research projects are typical examples of research environments where large amounts of scientific knowledge of this type are produced.

Stone conservation has taken and will continue to take great advantage of them, but the benefit can still be increased with a better framing of the research objectives and a clearer understanding of what type of validation is involved. All scientifically sound research results can lead to practical benefits for the stone conservation profession in the short or long term, but authors should refrain from suggesting hypothetical practical recommendations when no direct validation is supporting them. Having good results obtained in a laboratory study carried out on some samples of a limestone is not enough to generalise and sustain that a particular product is suitable for consolidating "limestones".

The studies considered here in this category will continue to be the main source of information for professionals directly involved in the practice of stone conservation, who will necessarily privilege the items that best fit their immediate concerns. Whether they consider them interesting or not will depend to a large extent on the care with which the information was structured and how it fits into the reasoning that professionals follow in their own practice. The discussion made in the previous chapter is intended to be a contribution to help scientists to follow a communication strategy that can facilitate professionals to read, understand and use the scientists' contributions.

4. CONCLUSIONS

Studies on stone consolidation are numerous, diversified, and coming from different research and professional contexts. Although they have their own objectives to fulfil, the perspective of contributing to the improvement of the stone conservation practice is common to all of them, whether in a short and direct path, or indirectly and in the long term. Whatever these studies may be, in terms of themes, depth and scope, they will be the source of information for professionals who will ultimately implement their scientific output.

Some of these studies deal with basic principles, theoretical issues or generic topics identified as relevant scientific questions not necessarily linked to any specific concrete situation. They produce scientific knowledge that will be reworked by other researchers and will eventually be incorporated into more practice-oriented studies. On the other side of the spectrum, practice-oriented research studies address real situations to find solutions to a concrete problem and their output will be a contribution to decision making to solve the problem.

Among these extreme situations, there is a vast set of research projects that are relevant producers of scientific information. Not infrequently, they follow ambiguous paths, jumping from the extreme of using theoretical and hypothetical approaches to propose practice-oriented "solutions" or "recommendations", without sufficient characterization of the practical situations they are implicitly addressing.

When the research focuses on any of the multiple variables of the consolidation process, the results may be closer to practical use, which may constitute one of the best ways to contribute to the improvement of the practice of stone conservation. Such an approach will not produce a direct "solution", but it has much greater chances of finding an end user capable of adapting it to solve a real conservation problem.

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Onsite assessment of subtle consolidation actions: can Shore durometers help?

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SUMMARY: From the few instruments available for the onsite assessment of stone resistance in heritage contexts, not many choices exist for the routine evaluation and/or monitoring of the effects of conservation products, particularly consolidants. Among the few available field methods, some are minor destructive, excessively complex and/or costly; some were developed for the measuring of relatively significant increments in stone resistance, and are not necessarily sensitive to small strength variations, such as the ones promoted by the consolidants with a higher compatibility with very porous decayed limestones, e.g. biomineralisation or nano limes. To understand if Shore durometers could support the onsite assessment of subtle consolidation actions, a Shore A and a Shore D were used to measure the surface hardness of decayed limestones. While the Shore D scale seems better suited for limestones than that of Shore A, measurement precision proved to be overly contingent of surface morphology.

KEY-WORDS: Soft limestones; subtle consolidation effects; onsite efficacy assessments; non-destructive testing; Shore durometers

1. INTRODUCTION

Research on biotechnological solutions for the consolidation of soft limestones applied in built heritage contexts has been steadily developing in the past decades. Among these solutions, microbially-induced carbonate precipitation (MICP) has gained increasing attention for the consolidation of decayed porous limestones both in outdoor and indoor environments, due not only to its physical-chemical compatibility with the stone substrates, but also given its de facto sustainable approach to heritage conservation (De Muynck et al. 2009).

Still, biomineralisation research has been largely carried out in laboratory conditions, and thus far reports on the outcomes of its application in conservation interventions have been scarce. While the compatibility of biomineralisation has been firmly established for the consolidation of soft decayed limestones and its (qualitative) onsite efficacy is clearly perceptible by operators (Delgado Rodrigues and Ferreira Pinto 2019), obtaining verifiable assessment or monitoring efficacy data entails considerable difficulties, since the few available non-destructive/micro-destructive testing (NDT) methods enabling onsite characterisation of subtle consolidation effects are insufficiently sensitive, not standardised and/or highly operator-dependent.

Current onsite/field NDT methods not requiring core samples and suitable for the direct assessment of stone surface resistance include the Drilling Resistance Measurement System (DRMS); the Scotch tape/peeling test; rebound measurements using Schmidt or Leeb sclerometers; and indentation measurements using durometers. Some of these methods are minor destructive and, except for the DRMS, none assesses below-surface effects, with many requiring a regular/even measuring surface. More importantly, most of these methods were developed for the measuring of relatively significant increments in stone resistance, and are not necessarily sensitive to small resistance variations, such as the ones promoted by MICP. Also, the substrates where biomineralisation solutions are advisable are typically very fragile (Delgado Rodrigues and Ferreira Pinto 2019) and may be entirely unable to withstand invasive testing.

Due to the subtlety of shifts in surface resistance, reported onsite MICP efficacy evaluations seem to largely resort to the peeling test (e.g. Rodriguez-Navarro 2015); but rebound or indentation methods have been shown to detect shifts in soft substrates and may be a relevant alternative for the ready assessment of the efficacy of MICP or other consolidants promoting generally slight increases in stone resistance. In this work, two Shore durometers were tested on a few weak limestones, to try and ascertain their applicability and limitations to the field testing of surface hardness in stone materials of cultural value.

2. CONTEXT

Subtly effective consolidants

Choosing a consolidation product for application on stone heritage is a “delicate problem” for which few satisfactory solutions exist (Delgado Rodrigues 2001). When dealing with cultural heritage materials, specifically during conservation interventions, the selection of consolidant products largely relies on the assessment of parameters that may typically be evaluated under the header ‘efficacy’ or under the header ‘compatibility’: if the product is not effective, there is of course no point in applying it, and compatibility – defined as the “extent to which one material can be used with another material without compromising the significance or the stability of the object” (European Committee for Standardization 2019) – is a chief mandatory requisite.

In practice, and although some proposals have been made (Sasse and Snethlage 1997; Delgado Rodrigues and Grossi 2007) there are no universally agreed limits – or even required assessment parameters – that a conservation product should verify before being considered compatible (Laurenzi Tabasso and Simon 2006), but, in essence, products used on cultural heritage materials should not introduce significant changes on the physical and chemical properties of the substrates they are meant to stabilise or otherwise preserve (Praticò *et al*. 2020), both in the short and in the long term.

In the consolidation of very porous limestones, the application of the compatibility requisite must be particularly stringent, since the consequences of introducing sharp modifications in the areas reached by the product may be critical to the point where affected areas form hardened scales and may be irretrievably lost (Sasse and Snethlage 1997; Delgado Rodrigues 2001; Delgado Rodrigues and Ferreira Pinto 2016). Thus, careful attention should be paid to properties related to water vapour permeability and resistance/strength, which should not dramatically shift with the introduction of the consolidant (Sasse and Snethlage 1997; Delgado Rodrigues and Grossi 2007). In the case of very porous limestones, efficacy, defined as “a measure of the strengthening effect of a consolidation treatment” (Delgado Rodrigues and Ferreira Pinto 2019, p. 83), should not be the main deciding factor.

In this perspective, Delgado Rodrigues and Ferreira Pinto (2019) recently suggested that the consolidation of very porous stones, including weak and decayed limestones, given the involved risks, i.e. “when harmfulness is the major concern” (2019, p.91), should be approached with compatibility as a guiding principle, “scaling up” the efficacy until a sensible result is possible – but not further. In practice, for very porous limestones, the suggestion would be to start with consolidants of “low incompatibility degree, even of foreseen low consolidation action” (Delgado Rodrigues and Ferreira Pinto 2019, p. 88), e.g. biomineralisation, barium hydroxide, ammonium oxalate, nano lime, lime water, ammonium phosphate (Delgado Rodrigues and Ferreira Pinto 2016), until surfaces are stabilised enough to allow other, less invasive, conservation actions.

The listed examples of “low incompatibility degree” consolidants are known to generally have very subtle strengthening effects and, even if their results are clear for the practitioners who use them, the measurement or quantification of these effects, which would support their validation and thus a more widespread use, is significantly hampered by the lack of onsite non-destructive/micro-destructive testing (NDT) methods sensitive enough to detect them.

Onsite efficacy assessments

Onsite product evaluations, in real exposure conditions, are necessary not only to ascertain and monitor both the efficacy and compatibility of the treatments carried out, but also the long-term evolution of the treated object. These evaluations should take place before, during and after the implementation of the conservation actions, and specially whenever particularly delicate actions – e.g. consolidation – are implemented.

In heritage contexts, testing is of course limited, not just practically – i.e. testing equipment must be portable in the case of immovable heritage – but also in principle – since heritage surfaces are generally very valuable, testing methods must be non-destructive or, at least – and depending on the value of the object – only minor destructive. However, and in spite of the outstanding development that conservation sciences have experienced in the past decades, onsite assessments of the performance of consolidation products are rare, particularly in the long term (Delgado Rodrigues and Ferreira Pinto 2019; Praticò *et al.* 2020; De Clerq *et al*. 2014).

At least partly, this lack of onsite assessments may be explained by the want of adequate, non-destructive, field testing equipment with sufficient precision (Drdácký 2018) and more or less readily available to practitioners and/or heritage authorities, which would enable, with the assistance of a conservation scientist, the implementation of regular testing programmes (Bläuer *et al.* 2012) – beneficial not only for the heritage object itself but evidently also for heritage conservation research (Teutonico *et al*. 1997).

Current field assessment NDT methods that are also reliable and more or less routinely available in stone conservation practice include water absorption via the Karsten pipe (RILEM TC 25-PEM) or the sponge (Tiano and Pardini 2004) methods; colour measurements using portable colorimeters; and surface resistance testing using the peeling test method (Drdácký *et al*. 2012). Ultrasonic velocity (see, for instance, Ahmad *et al.* 2009) and drilling resistance measurements (see Tiano *et al*. 2000 or e.g. Ferreira Pinto and Delgado Rodrigues 2004 for limestone consolidation applications) are also commonly employed for the onsite testing of stone heritage, but both will require specialist equipment and specific expertise for conducting the test and interpreting its results (Svahn 2006), making them a less attractive alternative for routine monitoring, particularly when attributed heritage values are not deemed high enough to justify the research investment.

Surface hardness measurements

From the more accessible tests listed above, water absorption and colour measurements are chiefly used to verify compatibility issues; whereas the peeling tape test can provide information on the efficacy of consolidants, even if just at surface level. In this sense, and regarding readily available surface resistance assessment methods, the peeling test filled a relevant gap for stone conservation practitioners and heritage authorities, in what it provides a simple quantifiable measurement that can easily be used for comparative evaluations such as before and after treatments; and short term / long term effects. It should nevertheless be noted that the peeling test provides information on surface cohesion, and does not necessarily inform on changes in superficial resistance that may be used in compatibility assessments, e.g. if an extremely hardened layer is formed as a result of consolidation. On the other hand, even when there is no risk of forming such a layer, as is the case with subtle consolidants, other surface resistance field assessment methods can be useful to complement the peeling test, as advisable in heritage conservation (Menendez 2016).

Hardness may be defined as a “subjective description of the resistance of an earth material to permanent deformation, particularly by indentation (impact) or abrasion (scratching)” (USDA 2012, p.4-4); it is “not a uniquely determined value, but a complex parameter, associated with the primary mechanical characteristics of materials (Gogolinskii 2019, p.1).

Surface hardness testing methods exist that are routinely used for the onsite characterisation of building materials or rock outcrops, including sclerometers and durometers, and that have been tentatively applied to heritage materials. These methods can chiefly be divided in rebound, indentation, and scratch methods, depending on measurement principle. In the sections below, a brief state of the art on the use of hardness field testing methods in stone heritage contexts is outlined; scratch methods were not included because all consulted sources referenced equipment which, albeit portable, does require core specimens to be extracted, which is seldom possible in high value surfaces.

Rebound methods

Rebound methods are among the most used in the onsite testing of built structures, particularly Schmidt and Leeb hammers/sclerometers. These devices measure surface hardness by assessing the rebound response of a spring-loaded (typically metal) mass impacting the surface to be measured at a predefined strength. The most widely used rebound method is arguably the Schmidt hammer, which computes rebound response from the distance covered by the mass after impact – the rebound value (R-value), varying on an arbitrary scale ranging from 10 to 100. Schmidt hammers are typically employed for the testing of concrete, but are also widely used in geomorphological research for the field assessment of rock hardness (Moses *et al.* 2014) – the R-value can be correlated with mechanical properties such as compressive strength (Goudie 2006; Aliabdo and Elmoaty 2012; Vasanelli *et al.* 2013), Young's modulus, and density (Katz *et al*. 2000; Aydin and Basu 2005), making it a useful tool for the monitoring of weathering progression (Aydin and Basu 2005; Mol 2014; Aoki and Matsukura 2007); Viles *et al*. further highlight its “speed, simplicity, portability, low cost and non-destructiveness” (2011, p.323). Nevertheless, all rebound methods are sensitive to the stone moisture content (Aydin and Basu 2005; Viles *et al.* 2011; Moses *et al*. 2014) and to the equipment operator (Viles *et al*. 2011).

From its use in different rock outcrops, Mol (2014) concluded that the N-type Schmidt hammer – the most common Schmidt sclerometer, with measuring ranges starting at 10MPa – was suitable for the testing of hard rocks e.g. granite (see also Aydin and Basu 2005), but softer lithotypes required the lower impact energy L-type Schmidt hammer, which is able to measure surface resistances starting at 5MPa – but will nevertheless leave a mark on the tested surface, even with the soft-surface mushroom adapter.

It should also be noted that Schmidt hammers suffer from the so-called 'edge effect', meaning that measurements will be affected "by the proximity of a rock edge or major crack" (Mol 2014, p. 5; see also Katz *et al*. 2000), including discontinuities such as those in "fissile, closely foliated and laminated rocks" (Goudie 2006, p. 704), and are therefore "not appropriate for the testing of fragile or severely weathered rock" (Aoki and Matsukura 2007, p. 1759), although Török (2003, 2008) was able to determine hardness differences caused by black-crust formation in limestones. Aydin and Basu (2005) furthermore reported some measurement scattering could occur in coarse-grained rocks due to "the influence of grain strength heterogeneity relative to the scale of probing area/volume" (2005, p.11), suggesting an increase in plunger tip diameter would minimise the effect.

Leeb sclerometers, in turn, measure rebound response by computing the velocities of the impacting mass before and after impact, expressed as the L-value, which can go up to 1000. Leeb sclerometers were originally developed for metal testing, but, perhaps because of their wide measurement range (Aoki and Matsukura 2007), their use in rock hardness and weathering research is nowadays widespread (Viles *et al.* 2011), even if it did not yet amass a body of supporting research literature comparable to that of the Schmidt hammer (Wilhelm *et al*. 2016).

While Viles *et al.* (2011) verified that the aforementioned 'edge effect' is less pronounced in the smaller Leeb sclerometer, and Aoki and Matsukura (2007) report its ability to assess stone weathering, Mol highlights its higher sensitiveness to "small scale irregularities such as edges and cracks" because of smaller impact bodies and lower impact energies, which may lead "to potentially a large variability in the data set" (Mol 2014, p. 5). Booth *et al.* (2012) were able to quantify clear hardness changes induced by subtle consolidants in artificially weathered Bath stone specimens; but Celik *et al*. (2020) report 'not great differences' and 'high data variability' when measuring the effects of tetraethylorthosilicates (TEOS) and diammonium hydrogen phosphate (DAP) in some selected Turkish stones. Wedekind *et al.* suggest that Leeb surface hardness can be used as a proxy for the *in loco* assessment of consolidation efficacy, albeit acknowledging that areas "highly affected by weathering and sanding were not measurable by the [Leeb] device" (Wedekind *et al.* 2016, p.496). Still, Zornoza-Indart and Lopez-Arce (2016) managed to assess the efficacy of silica nanoparticles in consolidating weathered Tunisian calcarenites exposed to different moisture conditions using Leeb hammer results (among other testing techniques), although standard deviations were quite high, particularly for the pre-treated samples. Likewise, Otero *et al.* (2021) integrated Leeb hardness measurements in the comparative efficacy assessment of different nanolime application protocols on weathered historical English limestone samples, also obtaining relatively high standard deviations.

Indentation methods (durometers)

Indentation methods perform static assessments of the surface hardness of materials by measuring the "pressure resisting plastic indentation by a comparatively strong and stiff indenter of well-defined geometry" (Hutchings 2009, p. 582). This resistance, or indentation hardness, is "inversely related to the penetration and dependent on the modulus of elasticity and the viscoelastic properties of the material" (Mohamed and Aggag, 2003, p. 251); and it is influenced by several factors, including indenter shape, applied force, and testing time. Depending on these factors, several indentation hardness testing methods exist, including the Vickers, Rockwell, and Brinell methods (see Broitman (2017) for a comprehensive overview), but most were designed as bench instruments (Gogolinskii *et al*. 2019), and most portable versions are quite costly (e.g. Vickers using ultrasonic contact impedance) and/or restrict the geometries of the objects to be tested (e.g. Rockwell or Brinell). From the available indentation hardness NDT field methods, Shore durometers (not to be confused with Shore sclerometers, which operate according to the rebound principle) are inexpensive and relatively easy to use, and their use has been spreading in stone conservation research.

Shore durometers measure surface hardness by applying a predefined pressure – via a calibrated spring – on a standardised indenting conical or spherical foot; the hardness value corresponds to the indentation depth, read on "a scale from 0 (for full penetration of the indenter) to 100 (corresponding to no penetration of the indenter)" (Broitman 2017, p. 22). Shore durometers vary not only on the indenter shape, but also according to the spring force, and therefore the measured value must always bear reference to the used device: the Shore A and the Shore D, by far the most common Shore durometers

(Herrmann 2011), apply forces of 8.1 N and 44.5 N, returning (hardness) values in HA and HD, respectively.

In recent years, Shore durometers have been frequently used for the assessment of consolidation results in built heritage materials, chiefly in lab specimen applications. Tavares *et al.* (2008), Matos *et al*. (2014), and Pascoal *et al*. (2015) were able to verify the consolidation effects of lime water and nanolimes on weak lime-based render specimens using Shore A durometers; with the exception of Matos *et al*. (2014), who present Shore hardness as sole effectiveness parameter, the durometer is used as a complementary technique. In Pascoal *et al.* (2015), Shore hardness results correspond to averages obtained from 12 measurements per specimen, albeit with “remarkable” standard deviations, which the authors attribute to “the intrinsic heterogeneity of the mortar specimens” (2015, p. 326). Tavares *et al.* (2008) obtained Shore A hardness values as low as 22 HA for historical mortars, but the remaining authors generally registered values in the 60 HA–90 HA range for non-historical mortar specimens.

Lánzon *et al*. (2019) used a Shore A to complement the Scotch tape test in the efficacy assessment of nanolime coatings applied on historical and non-historical earth plasters, with a relative standard deviation (RSD) of around half the average hardness value increment. Similarly, Faria *et al*. (2014) and Santos *et al*. (2019) used a Shore A in combination with a pendulum hammer to assess the surface hardness of earth plasters applied in different masonry substrates, obtaining RSDs of around 10%. In turn, Rodrigues *et al*. (2021a, 2021b) resorted to a Shore A for the comparative evaluation of ‘calcite blends’, a mixture of consolidating sols with calcite powder, as a decision-support tool for the selection of sols to be subsequently tested in stone samples.

When evaluations involve stone surfaces, the found indentation hardness testing examples mostly resort to Shore D durometers, following the recommendation of using Shore D in specimens with hardness above 80 HA (Herrmann 2011). Sena da Fonseca *et al.* (2021) recently undertook an extensive characterisation of fresh Ançã (soft) limestones, including mechanical properties using diverse methods, having found “a very good linear correlation between drilling resistance and shore [D] hardness” (2021, p.8), and “a direct relation between most physical and mechanical properties, as shown […] between open porosity (P_o) or coefficient of capillarity (CC) and hardness (HD)” (2021, p.10). Buj and Gisbert (2006) used a Shore D for the assessment of consolidants applied on three Spanish sandstones, reporting average hardness increments between 0.95% and 6.51% obtained from 50 measurements/sample. Together with ultrasonic wave velocity and uniaxial and triaxial compression strength, Chen *et al*. (2016) included Shore D hardness in the mechanical testing parameters for the assessment of potassium silicate as the consolidant of a porous Chinese sandstone; five Shore D measurements per sample were obtained, from which the authors reported average hardness increments between 1.1% and 4.5%, although the RSDs are very close to the lower increments (around 1%).

Rodrigues *et al*. (2021a) resorted to a Shore D durometer to complement drilling resistance data in the efficacy and compatibility assessments of modified alkoxysilanes applied on a soft Portuguese (Ançã) limestone – the authors logged at least 18 measurements/specimen, to compare average values to those obtained with the DRMS in the superficial millimetres, in order to ascertain the eventual development of a hardened surface layer. Following a similar testing methodology, including Shore D testing protocol, the authors furthermore assessed the efficacy and compatibility of base-catalysed TEOS as soft limestone consolidants (Rodrigues *et al*. 2021b). In these works, Rodrigues *et al*. (2021a, 2021b) obtained hardness values generally ranging between 87 HD and 95 HD – including the untreated (Ançã) stone samples –, with maximum RSDs of around 2%.

Meléndez-Zamudio *et al*. (2021) employed a Shore D as single resistance / hardness measurement technique for the assessment of modified alkoxysilanes applied in Mexican historical stone samples, measured in 4 points; the authors converted the average Shore D values to Brinell values, and these to values in the Mohs scale, to ascertain the efficacy of the tested consolidants. Still in the topic of alkoxysilane consolidants assessment, Briffa *et al.* (2012) used a Shore D0 (same spring force as the Shore D, but with a round indenter) as sole efficacy testing technique for the evaluation of TEOS-based products applied on Globigerina limestone, reporting ‘noticeable trends’ in spite of ‘minimal differences’ in hardness values – all average values (number of measurements not disclosed) ranged above 94 HD0, with standard deviations very close in value to the measured value increases. In turn, Xu and Li (2017) used a Shore D to measure pressed limestone powder samples – to mimic weathered stone – treated with different DAP consolidating solutions. Shore D hardness complemented the peeling test in the evaluation of surface resistance parameters, and was assessed from 5 measurements/sample, yielding average value increments above 38% for the treated specimens and notably low standard deviations (maximum RSD of 1%).

Not strictly linked with heritage applications, Barbero-Barrera *et al*. (2020) used a Shore D, together with ultrasonic and flexural and compressive strength testing, in the assessment of the mechanical effect of natural hydraulic lime as a stabiliser of compressed earth blocks. The authors recorded 18 measurements per sample, values ranging between 50 HD and 62 HD, with RSDs of ~10%. Similarly, Zhang *et al.* (2021) chose a Shore D to evaluate the hardness imparted by the addition of egg-white to lime and lime-tile dust mortars in different curing conditions; the method was complemented by compressive strength tests, and allowed measurements between 4 HD and 62 HD, with a maximum RSD of ~10%, obtained from 6 readings per sample.

Among the surveyed literature, only one source was found resorting to the Shore D durometer for field work in the scope of heritage materials science: Sutti *et al*. (2019) undertook the onsite hardness measurement of historical coating mortars as part of a characterisation programme that also included lab testing with a (bench) Shore C durometer (same spring force as the Shore D, but with a truncated cone indenter) validating field measurement averages; it is worth noting that all field measurements' RSDs were above 15%, for reported hardness averages between 36 HD and 57 HD.

From the consulted works, it is clear that durometers should, in principle, be an adequate solution for surface hardness testing of stones used in heritage contexts, even if typically used as a complementary technique. The RSDs, taken here as a measure of uncertainty, seem to be quite high for heterogenous materials, such as mortars, but generally lower for stone specimens; it is worth remarking, however, that no examples were found that included the (field or lab) testing of heterogenous stone surfaces, which is often the case when decay patterns call for a consolidation action.

3. MATERIALS AND METHODS

Materials and equipment

Two Shore durometers were tried for the assessment of surface hardness in a few Portuguese stone cube samples, typically employed in heritage buildings, that frequently exhibit deterioration patterns related to their relatively high porosity values / lack of resistance. The samples (Figure 1) included: Ançã (A) and Boiça (B) limestones, both almost entirely composed of calcite; and two dolomite stones, one from Coimbra (D) and one from Lisbon (M). Information on the open porosity and compression resistance of the tested samples is displayed in Table 1; other basic properties of the selected stones may be found in Ferreira Pinto and Delgado Rodrigues (2004, 2008).

Figure 1: Tested stone samples.

Table 1: Open porosity and compressive strength of the tested samples (adapted from Ferreira Pinto and Delgado Rodrigues 2004).

Stone	Open porosity (%)	Compressive strength (MPa)
Ançã	27	36
Boiça	10	135
Coimbra	18	89
Lisbon	15	143

Apart from a sample of (fresh) Ançã, all stone samples had been subjected to salt weathering, and generally presented surface loss in various degrees of severity. In terms of surface morphology, i.e. judging solely from surface features, samples could be ordered from *most regular* to *least regular* as follows:

- Ançã (A): Fresh Ançã > 2A90 ≥ 2A14
- Boiça (B): 1B20 > 1B18
- Coimbra dolostone (D): 1D66 > 1D68 ≥ 1D57
- Lisbon Miocene dolostone (M): 2M4 > 2M2 > 2M33

Method

Hardness measurements were obtained using two Shore durometers:

- a Sauter HD Professional Shore A HDA100-1 digital hardness tester (Balingen, Germany): standardised hardened steel indenting foot (35º cone); resolution 0,1/100;
- a Sauter HB Compact handheld Shore D HBD100-0 analogue hardness tester (Balingen, Germany) with drag indicator: standardised hardened steel indenting foot (30º cone); resolution 1/100.

The number of measurements varied between 5 and 22, depending on perceived variability and/or available testing area, which was quite limited for the most weathered specimens, namely the Coimbra dolostone samples. The Shore A was used in all stone samples. The Shore D, in turn, was only used in the Ançã and Coimbra stones, as follows: measurements were firstly taken on dry specimens; then, the sample surfaces were sprayed with water (becoming wet, albeit not soaked), to try and mimic changes in surface hardness akin to those induced by subtle consolidation effects, and new measurements were taken.

4. RESULTS AND DISCUSSION

Shore A

The first testing campaign used a Shore A digital durometer to try and ascertain the sensitivity of the equipment to differences in surface hardness in the aforementioned specimens, which showed different weathering degrees. However, almost all obtained values reached the upper end of the hardness scale, suggesting that the stones were generally too hard for the durometer to be able to distinguish minor differences. More importantly, the measurements spanned across a relatively wide range of values, with RSDs reaching almost 13% (Figure 2), indicating that small changes in hardness would probably fall within measurement error.

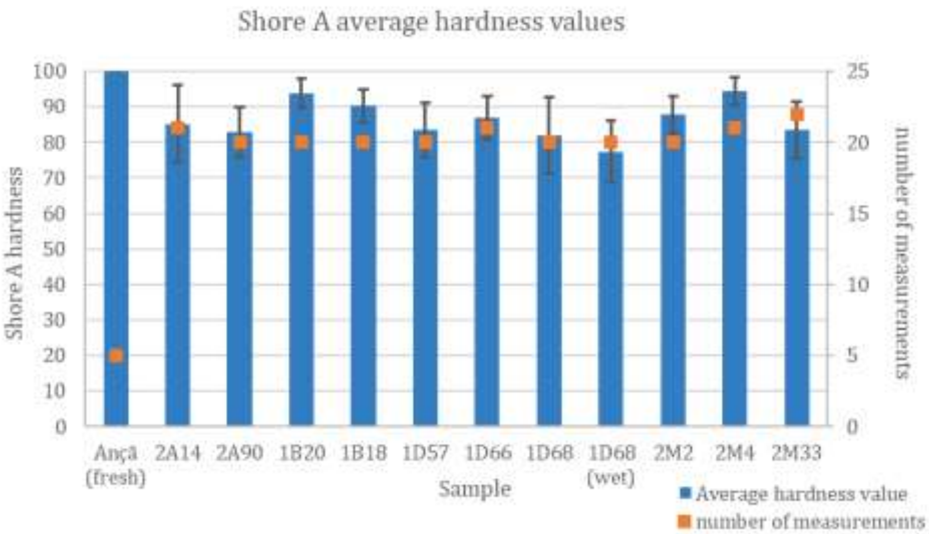

Figure 2: Average Shore A hardness values of a few selected stone samples. Values were generally above 80 HA, and standard deviations (in the error bars) varied between 0 HA (for the fresh Ançã) and 10.94 HA (for the 2A14 Ançã limestone).

Testing additionally proved that the disparity in hardness values, here assessed via standard deviation, negatively depends on the regularity of the surfaces, i.e., the testing is strongly influenced by the heterogeneity of the area where the durometer plate will sit when the measurement is taken (~2.54469cm^2). This means that a sufficiently wide regular surface area must be available for reliable results to be obtained, which may prove difficult in the case of sculptures and/or stone surfaces affected by material loss.

Given the obtained values, all generally reaching the upper limit of the Shore A scale, it was decided to test the samples with a Shore D durometer. Shore D is used for the measurement of harder materials (than those typically assessed with a Shore A) and it was expected that the stone hardness values would fall lower in the scale but still allow the identification of slight hardness differences, even if the Shore D scale is less fine than the Shore A scale.

Shore D

Tests with the Shore D analogue durometer were only performed in the Ançã limestone (A) and in the Coimbra dolostone (D) specimens; all samples were measured before and after water spraying, which intended to induce a slight shift in surface hardness.

Obtained hardness values (Figure 3) did not surpass 85 HD, apparently indicating that the Shore D scale is more adequate to assess stones – even those generally labelled as soft stones – than Shore A. However, the variability of the measurements was still very high, and again connected with the irregularity of the surfaces – dolostone samples, displaying the most irregular surfaces, were the ones with higher standard deviations.

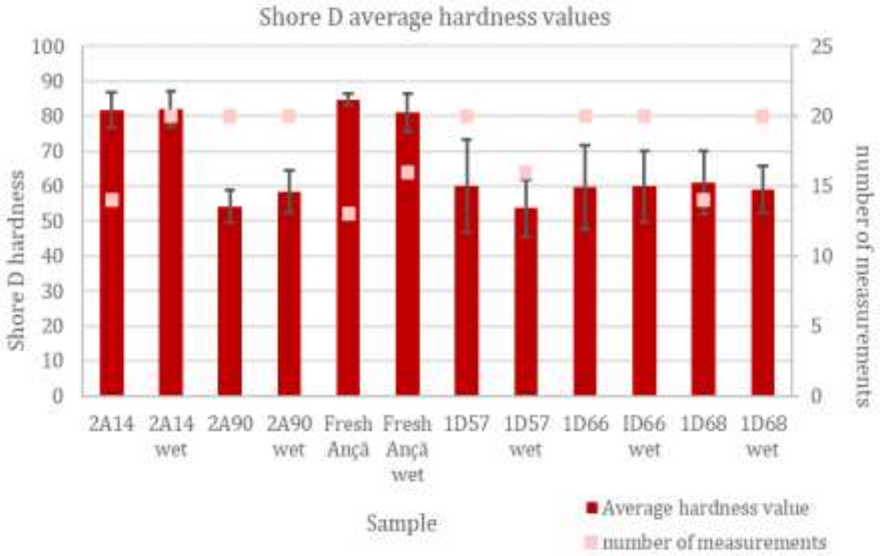

Figure 3: Average Shore D hardness values of a few selected stone samples. All values are below 90 HD, and standard deviations (in the error bars) varied between 1.65 HD (for the fresh Ançã) and 13.44 HD (for the 1D57 dolostone).

Looking at the obtained results, it is possible to conclude that:

- the Shore D durometer was unable to signal differences among the dolostone samples, wet or dry: average values are very close and standard deviations are the highest measured (varying between 6.73 HD for the 1D68 wet specimen and 13.44 HD for the 1D57 dry specimen);
- on average, value differences between wet and dry samples are generally very slight and mostly fall within the standard deviation limits (given by the error bars); nevertheless, it is noted that specimens 2A14, 2A90, and 1D57 showed slightly higher hardness values after wetting;
- in the dolostone samples, wet surfaces displayed lower standard deviations than the dry surfaces; in the Ançã samples, the opposite occurred;
- in spite of the apparently more irregular condition of 2A14, standard deviations for both weathered Ançã (wet or dry) specimens are similar; furthermore, the surface hardness of 2A14 was notably higher than that of 2A90, and was barely distinguishable from the fresh Ançã values;

Different Shore hardness scales are not directly comparable, nor easily relatable. Still, confronting the values obtained in the two sets of measurements (Figure 4) makes it clear that standard deviations were:

- for Ançã: generally lower than those obtained for the dolostone; furthermore, generally higher with the Shore A than with the Shore D;
- for the dolostone: generally higher with the Shore D than with the Shore A.

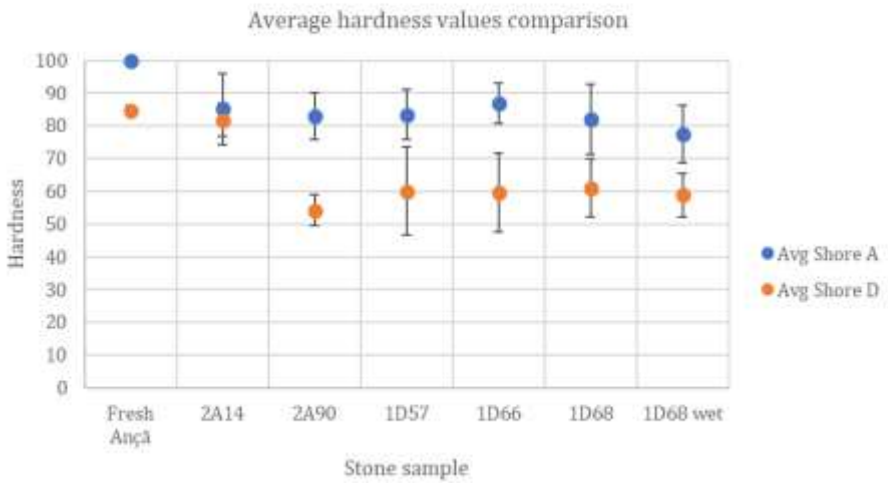

Figure 4: Comparison between average hardness values obtained with the two Shore durometers: Shore D seems to be less sensitive to small changes in surface hardness and more sensitive to rugged surface morphologies.

Differences in value dispersion between the stone types should, in principle, match differences in surface morphologies. This matching proved generally true for the Shore D measurements, with the dolostones presenting higher value dispersions than the Ançã specimens; even though the standard deviation for 1D66 was higher than that of the apparently more irregular 1D68 specimen. The Shore A, conversely, had overall comparable standard deviations for all stone types – fresh Ançã excluded –, varying between 6.10 and 10.94, with no clear connection to surface morphology, perhaps because the measurement range was too high up the Shore A scale to provide reliable results. On the other hand, the more precise (digital) Shore A durometer generally allowed less value dispersion than the (analogue) Shore D durometer, arguably because the slightly sharper tip of the Shore D causes it to be more sensitive to surface morphology.

One final word to acknowledge the much higher standard deviations verified in these testing campaigns when compared to the results in the surveyed literature for stone testing – the RSDs obtained here are comparable to those measured in mortar samples. The more likely explanation for this disparity seems to reside in the use of a portable device – as opposed to the bench instruments used in most surveyed sources – as well as in the absence of weathered or otherwise irregular stone surface specimens in the consulted works.

5. CONCLUSIONS

The onsite assessment of heritage objects is crucial not only for the correct planning and designing of conservation interventions, but also for long-term monitoring of the impacts of such interventions, as well as to improve our knowledge on conservation solutions. However, when it comes to assessing the effects of consolidation actions, simple and straightforward NDT field methods are scarce, and not necessarily sensitive enough to capture the often times desirably subtle shifts in resistance imparted to the stone by the consolidant. The work presented here stemmed from an attempt at ascertaining the applicability of Shore durometers for the assessment of slight shifts in the surface hardness of soft limestones, akin to those typically promoted by the use of high-compatibility but low-strengthening consolidants.

Testing the Shore durometers showed that the Shore A scale does not fare well in identifying surface hardness differences, since values will easily reach the top of the scale, even for (relatively) low-resistance stones. In this regard, the Shore D was more adequate, with most of the tested stones more spread in the upper half of the hardness scale. However, both durometers, and particularly the Shore D, proved very sensitive to surface morphology, which caused measurements to decrease in precision as surfaces became more irregular. On average, the durometers were able to identify differences between wet and dry samples, but these differences may be argued to fall within analytical error, and therefore further trials are necessary in order to understand if measurement protocols may be defined that allow more reliable results.

Lack of precision notwithstanding, it is also possible the superficial water spraying was insufficient to create noticeable differences in surface hardness, and therefore further testing with the Shore D durometer should be carried out, preferably using larger measurement areas, e.g. on samples allowed larger periods of water absorption.

Finally, it should also be noted that both durometers, and particularly the sharper tip of the Shore D, imprint a small indentation on the sample with every measurement, caused by the pressure of the tip, which may pose a problem when measuring very valuable surfaces and/or in the presence of detachment phenomena (e.g. scaling, peeling, splintering, chipping, etc.)

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Testing to assess the long-term durability of stone treatments. Limitations, misconceptions, and the harsh reality

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SUMMARY: Assessing the suitability of a treatment to be applied to a stone surface with severe loss of cohesion is always a major challenge; few satisfactory options have been proposed and sufficiently demonstrated, and the guiding principles on how to test, evaluate and decide on a stone consolidation treatment are still insufficient to be of real help to decision makers and professionals. On the best suited situations where some experimental work can be carried to help on this assessment, artificial ageing tests have been the most frequent option to gather information about the potential long-term behaviour of consolidation treatments. Exposure trials under outdoor conditions are generally considered to be closer to reality and the results tend to be taken as better indicators of the performance of real treated stone surfaces, but they also have significant bias to represent reality and to be safe estimators of future performances. Monitoring real treatments could be an alternative way to identify and characterise long-term performances, but the examples available are scarce and most of the time of limited interest and of short validity range. In this paper, the authors revisit the results obtained with outdoor exposure trials and compare them with tests done directly on real exposed surfaces and use information taken from artificial ageing tests to integrate into a comprehensive interpretation of different forms of evaluation in order to discuss whether (and how) these tests can effectively lead to an adequate assessment of the long-term behaviour of consolidated stones.

KEY-WORDS: stone treatment; durability; testing; consolidation; effectiveness; compatibility

1. INTRODUCTION

Assessing the suitability of a treatment to be applied to a stone surface with severe loss of cohesion is always a major challenge; few satisfactory options have been proposed and sufficiently demonstrated, and the guiding principles on how to test, evaluate and decide on a stone consolidation treatment are still insufficient to be of real help to decision makers and professionals.

The evaluation of immediate effectiveness and harmfulness are the most studied components. Although a large amount of scientific research has been reported, studies with a broader and full approach on these issues are scarce. Most of the time, these assessments are based on laboratory tests that do not fully address the relevant characteristics and are carried out on specimens made of recently extracted stones and, therefore, their results have significant limitations when deciding what treatment to apply to a deteriorated surface of cultural significance.

The assessment of immediate effectiveness is a first and important "screening" step, but in addition to the obvious consequence that a notorious ineffective treatment can be immediately and rightly discarded, this information can be of little value for the overall assessment of a consolidation treatment for a specific conservation purpose, unless a deeper discussion of the consolidation action and its consequences is carried out. Since some cohesion effect is expected to be re-established and a strength increment obtained, the level of reinforcement introduced can subliminally be taken as a measure of effectiveness. However, in practical terms, "stronger" is not synonymous with "more effective" or "more suitable", while a "weaker" consolidation treatment may well be enough to adequately resolve a deterioration problem.

The assessment of potential harmfulness is of far greater importance, although it is rarely considered as such. In fact, while the loss of effectiveness (translated as an insufficient cohesion increment) could in the end be compensated by the application of a new treatment, a problem caused by excessive destructiveness tends to be difficult to overcome or even irreparable. The evaluation of potential harmfulness also encounters much greater difficulties. Except for the evaluation of colour changes, which is a very simple procedure, the harmfulness is assessed indirectly, analysing the changes in certain measured properties, such as water absorption, water vapour permeability and others.

Defining "how much is too much" for each parameter and how to combine information from various parameters is a complex and difficult task, and we are still far from having a general consensus on how to process such information, although some contributions are already available and can be used as general guidelines in the meanwhile (Sasse and Snethlage 1996), (Delgado Rodrigues and Grossi 2007).

The evaluation of real cases is also not easy to carry out, as the harmfulness can take some time to be evident and when it reaches a sufficiently high impact, the overall performance of the stone consolidation treatment can be totally compromised. Contrary to what happens with a "weak" consolidation treatment, a harmful treatment has no return and the available alternatives, which possibly include some mitigation approaches, are surely unable of reversing the negative impacts needed to reach the initial condition.

The long-term behaviour of a consolidation treatment is often called durability, but this concept is poorly defined and can lead to ambiguous interpretations. For example, a strong treatment can fail because it creates a very hard crust that induces the formation of a plaque, which eventually will detach and fall off. In such a situation, the consolidation action of the treated layer can stay close to its initial level, which means that the consolidation action is stable, but the failure occurred because of an excessive degree of incompatibility that culminated in delayed harmfulness and the consequent loss of material. A consolidant with this behaviour could be described as having a "durable" consolidation action, although exhibiting side effects (due to incompatible behaviour) that makes it unsuitable for that specific use.

Artificial ageing tests have been the most frequent option to gather information about the potential long-term behaviour. They aim to accelerate the action of decay agents and reduce the time required to obtain meaningful information on the long-term performance of stone consolidants. In this type of tests, most variables are strongly distorted, the time scale is accelerated, but the transformation factor is unknown, the stone specimens are not sufficiently representative of exposed natural surfaces and all these deficiencies lead to results that are virtually impossible to extrapolate for the real-time behaviour of exposed stone surfaces. For this reason, it is quite common to see reports of these tests concluding that treatment A performed "better" than treatments B and C, but without giving any indication of how long in real conditions this test would correspond and without guaranteeing that this "better" performance will lead to safe use for a given practical application.

Exposure trials under outdoor conditions are generally considered to be closer to reality and the results tend to be taken as better indicators of the performance of real treated stone surfaces. Decay agents tend to be maintained to a great extent, but the shape and size of specimens and the exposure conditions are still sufficiently distinct from the actual surfaces to significantly weaken the conclusions reached with them. Furthermore, the fact that "*… the results that can be obtained by exposing treated samples outdoors are valid in just one set of climatic conditions…*" (Price 1996), limits the range for extrapolation.

Despite the inherent limitations they might have, artificial ageing tests can be useful tools to obtain information regarding the comparative behaviour of treated and untreated materials, and although they do not allow to fully anticipate the long-term performance of the treatments under study, they may shed some light on specific questions and thus contribute to better model and interpret long-term performances.

Monitoring real treatments could be an alternative way to identify and characterise long-term performances, but the examples available are scarce and most of the time of limited interest and short validity range. Results obtained in real cases may be difficult to compare with the reference situations for insufficient or obsolete information and they can hardly be directly extrapolated to different situations. As natural materials, stones always behave differently from each other, even when they are of a similar rock type; the shape and size of the stone objects and exposure boundary conditions are different, as well as the deterioration factors, namely in terms of type, intensity, and variation rates of the relevant decay agents. Although with limitations, monitoring of real treatments can add valuable information when properly searched and integrated.

In this paper, the authors revisit the results obtained with outdoor exposure trials and compare them with tests done directly on real exposed surfaces and use information on artificial ageing tests to integrate into a comprehensive interpretation of different forms of evaluation in order to discuss whether (and how) these tests can effectively lead to an adequate assessment of the long-term behaviour of consolidated stones.

2. MATERIALS AND METHODOLOGICAL APPROACH

Comparing results of ageing tests of stone specimens implies the integration of multiple parameters, including the natural intrinsic stone properties, the shape and size of the stone specimens, the environmental components, and the exposure conditions. Besides the difficulties induced by such a large number of variables, some of these variables also have a scale factor of unknown consequences. For instance, it is known that size and shape influence the results obtained in ageing tests, but it is not known to what extent and in what scale such results are modified; similarly, temperature can affect the end results, but the acceleration (or deceleration) rate is not known. To minimise these limitations, the intrinsic properties were levelled out using the same two types of stones for the analysis carried out here. With the same purpose, two consolidation products were considered. Validation in real exposed pieces of cultural heritage objects were used as benchmarking for the artificial ageing tests and natural exposure trials.

The two stone types are the "Ançã stone" and the "Coimbra dolostone". The "Ançã stone", herewith also labelled as AS, is a fine grained, micritic limestone, almost exclusively composed of microcrystalline calcite. Its porosity can range from 26 to 29% and the pore size distribution is unimodal with a relatively narrow radius ranging between 0.1 to 1 μm (Figs. 1, 2). The "Coimbra dolostone", herewith also designated as CD, is a very heterogeneous stone, mostly composed of dolomite (a Ca-Mg carbonate), with minor amounts of clays and iron oxides. It is fine grained, with frequent calcite veinlets and conspicuous vacuoles. It has undergone an uneven dolomitisation process that left relevant fingerprints in the porosity and cohesion variations identifiable at a centimetre scale. The pore radius ranges from 0.01 to 1 μm while its total porosity ranges from 14% to 19% (Figs. 1&2). The representative pore size distributions of the more heterogeneous and less porous areas of the stone of Coimbra (CD-Z2) suggest that its pore network has pores larger than those existing in its more porous areas (CD-Z1), Fig. 2. This stone also has wide variations in its physical and mechanical properties, whereas Ançã stone is far more homogeneous, as can be observed in Fig. 3. For additional information of the properties of these lithotypes, see also (Ferreira Pinto 2002) and (Ferreira Pinto and Delgado Rodrigues 2008).

Fig. 1 – Aspect of "Ançã stone" in the Renaissance portal of Santa Cruz church, Coimbra (left), and of "Coimbra dolostone" in the Santa Clara old convent, Coimbra (right).

These two stone varieties were tested with two consolidation products. An ethyl silicate in white spirit, ready to use (Tegovakon V, from Goldschmidt) and an acrylic resin based on an ethyl-methyl- acrylate copolymer (Paraloid B72, from Röhm and Haas) applied with the following formulation: 0.06/0.61/0.09/0.2 = resin/toluene/xylene/acetone. Application of both products on site was made by brush, twice in the same day and until apparent refusal. The ethyl silicate was re-applied two days after the first application. Detailed information about the products and treatments can be found in (Delgado Rodrigues, Ferreira Pinto, and Costa 2002) and (Ferreira Pinto and Delgado Rodrigues 2008). Information on the treatment protocols used in laboratory conditions will be described along the text when appropriate.

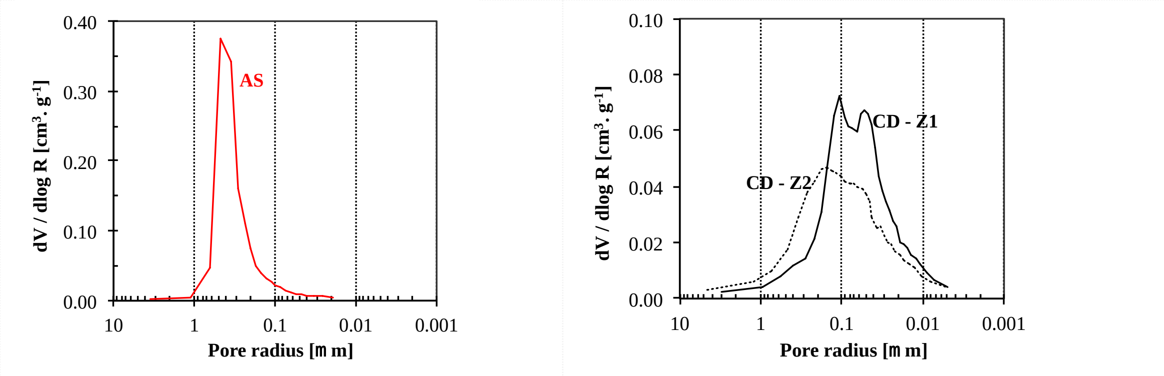

Fig. 2 – Representative pore size distributions of AS and DC stones. Data taken from (Ferreira Pinto 2002)

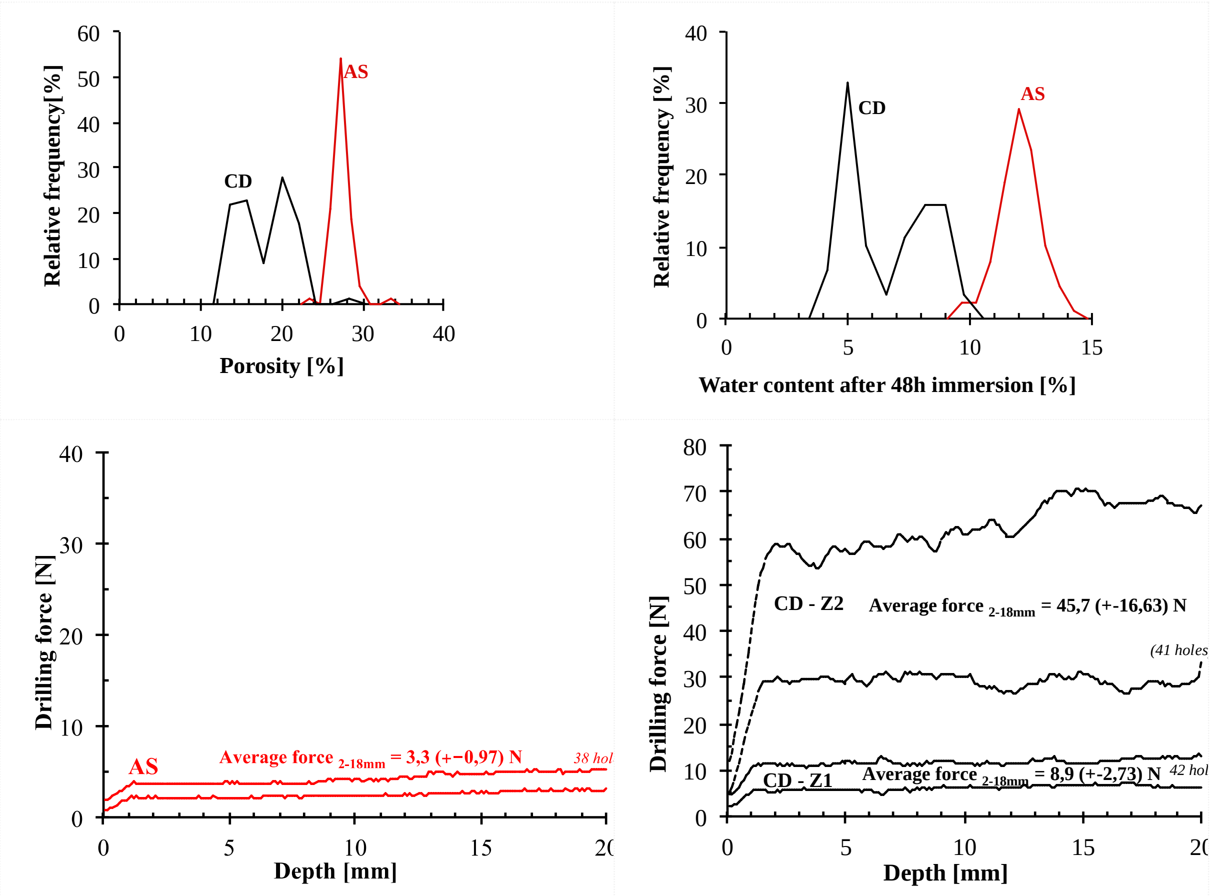

Fig. 3 – Typical variation ranges of some physical and mechanical properties of AS and CD stones. Data taken from (Ferreira Pinto 2002)

Over the past 25 years, the authors have tested these two types of stones and consolidation products under various protocols for a variety of purposes (Fig. 4). As a different purpose requires a different approach, this can end up leaving a lot of information that, while it may be intrinsically coherent, is scattered and difficult to integrate into a comprehensive understanding. In the meantime, the authors' experience has changed and their views on the first approaches then followed may no longer be in line with the new knowledge available, nor compatible with current perspectives on these testing methodologies.

With such diverse forms, published data tends to be read as individual and disconnected pieces of research, since it can be reasonably expected that only the authors would be willing to uncover hidden connections and draw consequences from such scattered pieces of research.

In this line, the methodology followed in the preparation of this text aimed to identify situations that could be compared for different ageing tests or outdoor exposure conditions and trace the interpretations that fit the data, trying to compare them with known real situations of heritage sites.

Fig. 4 – Example of outdoor exposure trial arrangements showing specimens of different sizes and shapes.

3. RESULTS AND DISCUSSION

A basic background on the testing of stone consolidants can be obtained in a few essential references (Sleater 1977), (Clifton and Frohnsdorff 1982), (Price 1996), (Sasse and Snethlage 1996), (Laurenzi Tabasso and Simon 2006). An important set of testing protocols can be found in (RILEM-25PEM 1980).

3.1 Test specimens; to what extent are size, shape, and surface condition decisive?

There is a basic perception that the size of the specimens used to test stone consolidants has relevant influence in the testing outcome, mainly dictated by the need of having specimens representative of the stone intrinsic characteristics. This is the minimum threshold of requirements for any testing purpose, but this requirement is not enough for defining the size of the specimens for testing stone consolidants, namely because "*…when the depth of penetration and bulk properties are considered important … the use of very small samples should be avoided*." (Laurenzi Tabasso and Simon 2006).

The scale effect of sample size can be analysed from multiple perspectives, and the application of a consolidation product itself is not immune to this scale effect. For instance, when studying the role of treatment procedures we have shown that the same (as far as feasible) application protocol had induced larger absorption values for larger surfaces under treatment, a situation especially clear for the more porous stone AS (Fig. 5) (Ferreira Pinto and Delgado Rodrigues 2008).

Having different sample sizes absorbing different amounts of products, it is expected that the results of subsequent tests may also be influenced. Often the authors resort to specimens of equal size when testing different products to avoid this scale effect, but even this fair premise is not enough to get around this issue. This can be easily perceived when testing consolidated specimens in compression tests. For instance, let us consider two consolidants, one capable of impregnating 10 and the other 2 mm in thickness, to be tested in compression tests in cubes with 3 or 5 cm side; the approximation to the characteristic value of the consolidated zone is different for both products depending on the size of the specimens, naturally with 3 cm side specimens giving better approximations in both products. However, the characteristic value of each product is not equally penalised when the specimen's size increases, with the product with the lowest penetration capacity being the most undervalued one.

Similar difficulties can be anticipated when it comes to exposure trials under outdoor conditions. Different impregnation depths will have distinct impacts on the decay of specimens with the same size, and, similarly, the same impregnation depth will have different impacts on the performance of specimens of different sizes.

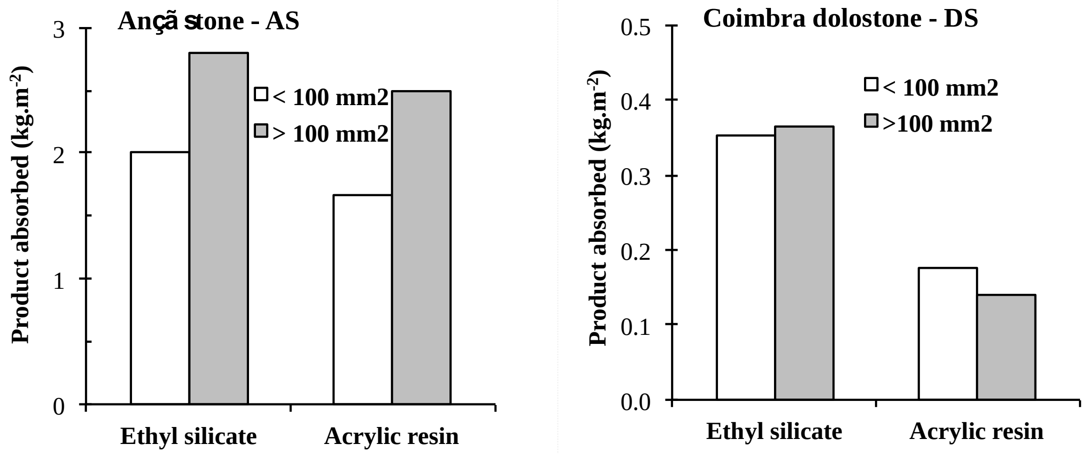

Fig. 5 – Influence of the surface dimensions on the amount of product absorbed. Application by brush until apparent refusal of an ethyl silicate and an acrylic resin. Data adapted from (Ferreira Pinto and Delgado Rodrigues 2008)

Size and shape of the exposed specimens influence the actions impacting in their boundaries (for example, the amount of radiant energy received or of rainwater absorbed or evaporated may be similar when expressed per unit area, but they will be different when expressed per unit volume) when taking the specimen envelope as the reference boundary, but the things can become even more complicated when the interface between the consolidated and the unconsolidated stone is considered. The location of this interface vis-à-vis the specimen boundaries will depend on the specimen size and shape which implies that the intensity of the environmental loads that will interact with this interface will also depend on the specimen's size and shape. For example, when drying a stone specimen not fully treated the water present in the untreated zone may cross the consolidated layer to escape to the atmosphere or it may take an easier path moving away from the consolidated layer to evaporate in the posterior surface of the specimen, depending on the boundary conditions defined by its size and shape.

Although exposure trials under outdoor conditions minimise the distortions to which deterioration mechanisms are subject in artificial ageing tests, they are still far from being a faithful representation of real cases. Therefore, it is very risky to adopt conclusions drawn to apply them directly to real situations, and even comparative analyses of results obtained with products or treatments may lack the necessary experimental conditions to have real validity.

The surface condition and the in-depth decay pattern of the specimen to be treated for testing are also big issues, possibly among the most important ones. Naturally decayed stones are difficult to find and are virtually inaccessible when a cultural object is in question. As a common alternative, specimens are sawn from blocks, meaning that their surface condition tends to be representative of the stone block, but not of the exposed stone surface. The preparation of artificially deteriorated stone specimens has been attempted, but experience shows that this is not a trivial task, as is deduced from the paucity of examples that have been published.

In a preceding work, we have tried to create artificially deteriorated limestone and sandstone specimens using salt crystallization and end up concluding that "*The preliminary tests have shown that the process was difficult to be mastered, since very rapidly, at least for the very porous materials, specimens pass from a sound condition to complete failure*." (Delgado Rodrigues, Ferreira Pinto, and Paulos Nunes 2007).

In addition to the difficulty in obtaining "realistic" decayed specimens, these specimens were all different from each other, which necessarily introduces one more parameter to be considered when making comparisons. The use of specimens sawn directly from blocks appears, therefore, as an unavoidable and unique alternative for testing stone consolidants. In such circumstances, it is not surprising that published literature on stone consolidation experiments have mostly used "un-deteriorated" sawn specimens, yet it is rare to see authors warning of the expected lack of representativeness their results may have when extrapolated to deteriorated and exposed stone surfaces.

In short, size, shape, surface condition, and in-depth decay are not only relevant factors to be taken into account when exposure trials under natural conditions are considered, but they can even make the results of serious and labour-intensive test programs difficult, if not impossible to be directly translated in applicable and effective conclusions when the consolidation of real deteriorated surfaces is in question.

3.2 What do exposure trials really evaluate?

Because of the closest similarity between the exposure environment and the environmental conditions affecting real objects, exposure trials under natural conditions are generally considered to provide the most accurate information about the expected performance that a consolidation treatment would exhibit once applied to a deteriorated stone of that object. As discussed in the text above, this direct extrapolation cannot be assumed as a simple exercise and any attempts to draw applicable conclusions must be made with extreme caution and under strict critical analysis.

A complicated first step arises when trying to understand the underlying meaning of the term “performance”. This term is commonly used to encompass a synthesis of various components that reflect the general behaviour of a given situation. For a consolidation treatment, it can cover the following partial behaviours:

i. The immediate and short-term effectiveness,
ii. The immediate and short-term harmfulness,
iii. The stability in time of the cohesion action (or long-term effectiveness),
iv. The delayed harmfulness.

A misbehaviour of any of these items is enough to impair the "performance" of the consolidated stone, and they need not necessarily degrade simultaneously, on the contrary, the treatments may happen to exhibit a satisfactory medium- or long-term combined effectiveness and a critical delayed harmfulness, which would imply an overall bad “performance”.

Understanding which of the performance components was impaired during an exposure trial is not always easy, but it is essential that the analyses performed should identify it. Delayed harmfulness tends to leave visible impacts, such as colour changes or detachment of surface fragments, while losses in effectiveness may require instrumental tools to verify them. Simultaneous impairment of efficacy and harmfulness is also not uncommon.

While it is doubtful that an exposure trial under outdoor conditions can constitute a satisfactory replication of the exposure conditions of a real object, the information they provide, if properly interpreted, can provide clues as to how a treatment on a real object might behave. For example, the formation and detachment of a plaque in an exposure trial may not be enough to rule out a treatment, but it could be interpreted as a serious warning that a potential critical interface between the treated and untreated layers is present. The occurrence of multiple scales may be insufficient to conclude on the duration of treatment, but it indicates that superficial deterioration is likely to occur. On the opposite side, a surface that resists the exposure test unaltered is a positive fact, but it is not sufficient to validate a treatment.

3.3 Testing with salts. Is it as simple as it sounds?

For decades, salt crystallization has been used to test the quality of stone materials and to predict how they will behave when incorporated into building components. The ASTM standard C88 is one of the salt crystallisation test paradigms. Research and testing bodies have used it in its original protocol or with minor or major modifications to test stone treatments, while the literature shows that virtually every researcher has their own variant of this test. Sodium sulphate and sodium chloride are the most used salts, while full immersion, partial immersion, and salt mist are the most popular application protocols.

Topics related to salt crystallisation constitute one of the domains most recurrently reported in the scientific literature (Evans 1970), (Arnold and Zehnder 1989), (Charola 2000), (Doehne and Price 2010). In the numerous studies and proposals available, the interpretation of the results of salt crystallization tests is essentially casuistic and the faithfulness with which they reproduce the real behaviour is far from being a demonstrated evidence. The type of salt and its concentration, the application protocol, the relative duration of the wetting and drying periods, the ambient temperature and its rise and fall rates, the size and shape of the sample, among others, are too many parameters to allow a complete control of the process and make its results meaningful and interpretable.

In a study carried out for the preparation of a conservation intervention, the authors were confronted with a highly porous stone (Ançã stone – AS) in a highly deteriorated state and in need of consolidation (Delgado

Rodrigues, Ferreira Pinto and Belém 1997). Salt crystallisation was identified as a prevalent decomposition process and dealing with a salt-laden substrate had to be faced as an inevitable fact.

While some light desalination might be feasible, full desalination could not be considered and therefore, some preparatory studies were carried out to see to what extent a salt-laden stone could accept a consolidation treatment. The research question was not only to see how well a treatment withstands a salt crystallization test, but also to assess whether a salt laden stone would accept a consolidation treatment.

For this, a sound Ançã (AS) stone block was first impregnated with a saturated solution of potassium nitrate (this was the main salt present in the building) and allowed to dry (Fig. 6). After a slight desalination of its upper surface, several treatments were applied by brushing in fields separated by a trench 1 cm deep. Treatments were applied as they are normally specified.

Figure 6 – Aspect of the AS block (28% porosity) treated with different products after forced percolation of a salt solution (left) and after removal of efflorescences (right). The central test area in the bottom row showing an intense salt blossoming is the zone treated with ethyl silicate. The central test area in the upper row was treated with Paraloid B72. The block is about 35 cm long

The block was sealed on its four side faces and water was forced to infiltrate from the bottom to evaporate through the treated upper surface. This mock-up intended to represent as faithfully as possible the conditions to which a consolidated surface would be subject in a real situation. As seen in Fig. 6, the salt solution actually crossed the treated areas and it was immediately clear that not all treatments allowed the salt to appear in similar amounts. Interestingly, the area treated with ethyl silicate, the main candidate for application, allowed the passage of the salt solution without inducing any visible damage, in marked contrast to the neighbouring areas treated with other consolidants and water repellents.

Why is this case relevant to the discussion here? In fact, ethyl silicate was applied in several areas of the monument, but unfortunately, conspicuous scales began to appear a few years after application, showing that the test procedure did not fully represent the real exposure conditions. Despite this insufficiency, the test allowed to discard other treatments that clearly showed to be potentially more harmful.

Similar onsite behaviour seems to have occurred with the Lecce stone (Calia et al. 2004) and was also already noticed in the pioneer work of (Bailey and Schaffer 1964), quoted in Wheeler (Wheeler 2005): "*On stone of relatively poor quality its [ethyl silicate] use has been followed by scaling of the treated surfaces*".

What can we learn from this case study? Despite the harsh test conditions (high salt content present in the block and the salt solution forced to cross the treated layer), the treated surface held up very well in contrast to the performance of real surfaces. The most obvious reason is the initial condition of the stone mock-up, which was a sound stone with a surface sawn directly from a block that obviously did not adequately represent how a naturally decayed stone would behave. Other relevant reasons, namely the occurrence of repeated cycles of dissolution and crystallisation of salts should have played a significant role in this process.

The surface condition has been widely considered as a very relevant issue; a fact that has not prevented that the vast majority of tests are usually carried out on freshly prepared surfaces. Given the notorious distortions that a newly prepared "perfect" surface introduces into the test output, the results produced under this test paradigm should always be questioned on the possible bias they may represent.

In a series of ageing tests carried out for a different project, consolidated specimens (5 cm side cubes) were subjected to an atmosphere of saline mist in a climatic chamber. Among the untreated specimens added as a reference, one was impregnated with salt in order to observe whether a high initial salt load would greatly influence the deterioration process. Surprisingly, this specimen went through the entire ageing cycle without any mass loss, unlike the others, treated and untreated, which showed some noticeable mass loss.

Such behaviour was then attributed to the impossibility of the salt mass to be dissolved and recrystallized within the time allowed for each step of wetting and drying. This situation could certainly have been foreseen when planning the test, as it is more or less obvious that dissolving a mass of salt present within a block is not similar to dissolving a thin layer of salt on the surface / subsurface of the specimen. However, despite its naivety, it illustrates how difficult it is to be certain about the degree to which our test conditions represent actual conditions of deterioration and how to translate our results into solving concrete problems.

3.4 Ageing tests, exposure under natural conditions, and onsite experiments. How far can we stretch the conclusions?

After a fairly extensive series of tests with the same stone and the same products under different test conditions, the difficulties to extract practical conclusions seem to increase each time one more test is added to the interpretation (Tables 1 & 2)).

The reduction of water absorption and increase of cohesion identified in almost the entire thickness of the stone slabs treated with TG and B72 treatments limited the percolation of saline solutions through the specimens and consequently the exposure to a marine environment for 4 years left only minor superficial damage (TG) or no visible damage (B72), while the exposure to a saline mist in a climatic chamber has induced some visible scaling and powdering. It is clear that the size and shape of the specimens, and the test conditions were very different in each test, therefore no indisputable conclusion about the suitability of ethyl silicate to consolidate this stone can reasonably be drawn from these results. From a research standpoint, we could certainly claim that these results are inconclusive, but if forced to wear practitioner's shoes, it would be unacceptable to conclude that way after three long and expensive "performance" tests. Possibly, it could be concluded that the ethyl silicate is adequate to consolidate the AS stone, noting, eventually, that certain minor superficial losses could eventually appear with time.

The ethyl consolidation treatment was also studied on deteriorated areas of real objects that needed to be consolidated. A column in the cloister of Celas Monastery (Coimbra, PT) and a balustrade in the gardens of Queluz Palace (Queluz, PT) were used for this purpose. Table 2 synthetises the results of interest for this analysis.

These images show that the results were quite unsatisfactory, and hardly anyone could conceive of applying this treatment after knowing the outcome of these tests. Whatever the reasons invoked to explain the results, not excluding that the implementation of the tests may have shortcomings, it seems clear that the path followed with the “performance” tests does not unequivocally lead to the resolution of the real problems of consolidation. The authors would be happy if their results were contradicted as unrealistic or inadequate and would like to be assured that practical decisions are made with more robust and focused tests than ours, but we would not be surprised if we are told that decisions are often done with results of this nature, if not worse.

The results obtained in tests performed with B72 were somewhat easier to interpret. Scaling and powdering were frequent and a thin plaque formed in some aging tests, suggesting that serious concern should be taken for granted if such consolidation were to be anticipated. An onsite test with Paraloid B72 carried out on a deteriorated parapet in the Celas Monastery developed a thin hard crust that soon showed to be poorly attached to the substrate and peeled off (Fig.7).

The dolostone characterised above (DS) is a very heterogeneous material that often exhibits differential erosion patterns and mass loss. All ageing tests done with ethyl silicate and Paraloid B72 showed signs of mass loss, forcing the conclusion that this type of stone is close to an "impossible" material to consolidate (Fig. 8).

The information briefly presented here can certainly be interpreted differently by our readers, but in our understanding only one conclusion could be drawn: neither ethyl silicate nor Paraloid B72 are safe solutions for consolidating this highly porous limestone (AS) nor the dolostone (DS). Knowing that ethyl silicate has been widely applied to consolidate deteriorated porous limestones, what went wrong here? Are our results and interpretation too drastic and overly conservative, or have we missed or gone beyond some critical step?

<table>
<tr><th colspan="2">Table 1 - Aspect of AS treated with ethyl silicate and B72 and submitted to outdoor exposure and artificial ageing tests</th></tr>
<tr><td>
</td><td>AS treated with ethyl silicate (lower central area) after forced percolation of a saline solution and subsequent washing of the formed efflorescences. The perfect condition of the surface treated with ethyl silicate after being submitted to a forced percolation of a saline solution could be interpreted as a demonstration that ethyl silicate is safe to be applied in this high porosity limestone (see also Fig. 6). The area treated with B72 (upper central area) showed scaling and non-negligible mass loss.</td></tr>
<tr><td>
</td><td>Cubic specimens (5 cm side) of the same stone (AS), with the lateral faces sealed until 1cm of the upper surface, treated by brushing until refusal with ethyl silicate (2A12 $_{TG}$) and with B72 (2A17 $_{B72}$) tested in a salt spray chamber. The ethyl silicate treated specimen showed powdering and mass losses, while the specimen treated with B72 showed intense scaling and mass loss.</td></tr>
<tr><td></td><td>2.5 cm thickness slab of this same stone treated by brushing until saturation with ethyl silicate showed little signs of surface degradation and reduction of superficial hardness after 4 years exposed in natural conditions near the sea.</td></tr>
<tr><td></td><td>2.5 cm thickness slab of this same stone treated by brushing until saturation with Paraloid B72 showed almost no superficial signs of deterioration after 4 years exposed in natural conditions near the sea.</td></tr>
</table>

<table>
<tr><td colspan="3">Table 2 – Deteriorated surfaces of AS stone treated with ethyl silicate</td></tr>
<tr><td></td><td></td><td>Column of AS before (left) and three years after (right) treatment with ethyl silicate. A significant mass loss was registered as a result of an acceleration of the pre-existing deterioration rate (Celas Monastery, Coimbra, Portugal).</td></tr>
<tr><td colspan="2">
</td><td>
</td></tr>
<tr><td colspan="3">Surface treated with ethyl silicate, one month and 6.5 years after treatment. The initially stable surface started showing conspicuous scaling affecting the entire surface (Gardens of Queluz Palace, PT)</td></tr>
</table>

Figure 7 – Parapet coping of AS stone treated with Paraloid B72. A thin crust formed and peeled off a few months after application

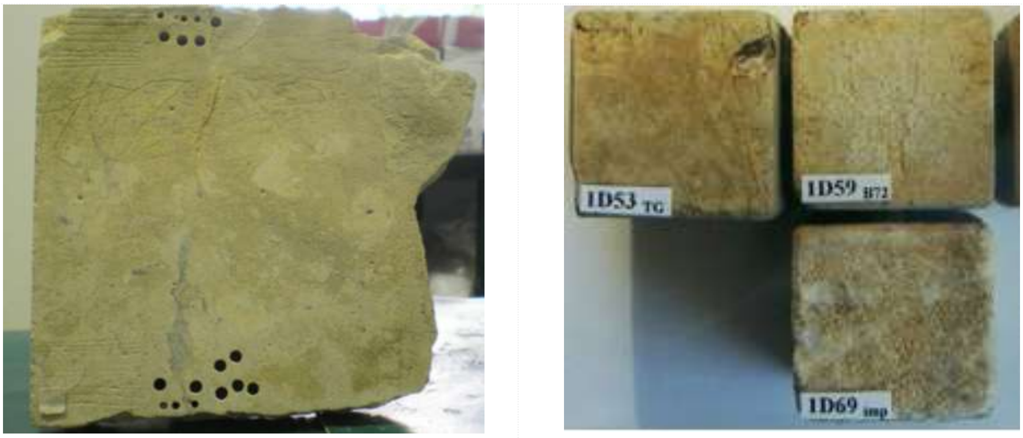

Figure 8 – Coimbra dolostone (CD) after ageing tests. 2.5 cm thickness slab treated by brushing until saturation with ethyl silicate and exposed to a marine environment for 4 years (left). Cubic specimens (5 cm side), with the lateral faces sealed until 1 cm from the upper surface, treated by brushing until refusal with ethyl silicate ($1D53_{TG}$) and with B72 ($1D59_{B72}$) tested in a salt spray chamber, (right). All specimens showed a certain surface recession

The difficulty of using laboratory data to make decisions about how to consolidate a stone object is not new and can be captured in the published literature. Studies that compare various products and treatment protocols and end up concluding that A is better than B and/or C are often evidence that a complete demonstration has not been made that A, in its own right, is a totally satisfactory product.

4. FINAL REMARKS AND CONCLUSION

The apparently pessimistic view that can be grasped from the above text may eventually lead to the idea that testing is superfluous, which is definitely not in the authors' perspective. On the contrary, testing is an essential step to gather information to support our decisions and reduce subjectivity, but it is also true that the results obtained from testing can be misleading and the conclusions erroneous and useless.

In general, it can be assumed that the quality of the tests and the accuracy of the research results meet the appropriate standards and that the test programs claim support in options followed in similar projects collected in the literature, which means that the results obtained, per se, meet the requirements to be published and, therefore, will not be questioned here. In contrast, conclusions and recommendations made with the aim of providing guidance for practical use are often speculative and unsupported by data, making them of little practical value, if not controversial and risky.

A clear understanding of what objectives are pursued and a proper planning to reach them will help to exclude temptations to "stretch" conclusions to demonstrate hypotheses that fall outside their domain of expertise. For example, a doctoral thesis that followed a well-executed research plan may well fulfil its objectives even if it leads to a dead end in terms of directly applicable practical conclusions, while it may be seriously compromised if the author, without insufficient mastery of the practical questions, is tempted (or pushed) to draw peremptory conclusions about the expected performance of the tested treatments applied on real stone objects or advance any recommendations for direct practical use.

Research and testing will benefit from better clarification of objectives, and possibly the way forward is to move progressively from synthetic approaches to testing to a more analytical way of decomposing reality that is overly complex into elementary "workable" questions. Testing to assess the overall performance of a consolidated stone object may have some chances of providing useful information, but such an approach tends to operate like a "black box" and the chances of understanding the processes involved and gaining strength to extrapolate to other situations will be minimum, if any.

When presenting its report in 1982, the US Committee on Historic Stone Buildings and Monuments stated that "… *we must determine if weathering can be recreated in the laboratory. The committee is not optimistic that this can be done*" (Anonymous 1982), and about a decade after, C. Price concluded that "…*reliable tests for predicting the long-term performance of conservation materials are still a long way off*" (Price 1996) . After forty years of worldwide research on this topic, many "*lab recreation*" exercises have been published, and today we could possibly conclude that "**...***we are not confident that any of our "recreations" adequately reproduce the deteriorating processes that act in situations of the real world*", and therefore, predicting long-term performance is still more of a wish than an achievable fact.

In their key paper, Laurenzi Tabasso and Simon (2006) conclude that "*The final aim of testing, as discussed so far, is to contribute to the conservation of porous building materials through the selection of products and tools for their treatment. It is, therefore, of the utmost importance that the adopted test methodologies <u>try to reproduce the field conditions as far as possible</u>, in order to yield results that are applicable to real cases.*" (our underlining), but this recommendation may only set a myth, which possibly with exceptions, will never be able to guarantee that the results of ageing trials are safe estimates of reality. If so, this would mean that researchers and practitioners might have to accept that they must work with more or less "objective" guesses and little with substantive reasoning and scientific evidence.

However, this is not the end of History, and by no means the end of stone consolidation tests. However, it may be time to call our attention to the need to change the paradigm that has been followed so far. Such paradigm is still to be defined, and the few followings hints aim at conveying the perception on how the authors look at the actual situation and how they would like to see the research community moving forward.

Questioning the usefulness of models and tests under complex environmental conditions to predict the "overall performance" of consolidated stones is probably one first step. Next, the complex concept of "performance" should be broken down into as many components as possible, which are to be tested individually and to be included in integrative reasoning or modelling, where feasible.

The evaluation of the effectiveness of a consolidation treatment can be done through a certain number of parameters (amount of absorbed product, amount of retained product, achievable impregnation depth and a parameter informing about the increase in cohesion) whose results will then be integrated in a logical interpretation, for example, adopting the *scaling up / scaling down* model, published elsewhere (Delgado Rodrigues and Ferreira Pinto 2019), or any other.

It is timely to recall that failures caused <u>exclusively</u> by insufficient cohesion increase are, in general, not very problematic and are not commonly reported. For instance, one application of lime wash on a sugaring marble would certainly correspond to an ineffective consolidation treatment, and this obvious failure to consolidate the deteriorated marble, if no harmfulness is present, could be seen as a "placebo". Since the needed increment in cohesion can vary from minimal values to high strength requirements, testing for effectiveness can be handled with the said measurable parameters and a simple reasoning model. Smaller cohesion increment needs will point to "softer" consolidants and/or lower amounts of product, while higher increments will require "stronger" products and/or higher amounts to be applied. With the knowledge that exists today about consolidation products and an adequate reasoning, it will certainly not be a problem to find a product capable of satisfying the necessary requirements to reach an adequate level of "effectiveness".

However, the serious problems that arise in consolidated stone objects do not result from an insufficient degree of "effectiveness", but rather from an excessive degree of "incompatibility", which can also be considered as a form of "delayed harmfulness". In fact, often, products of greater "effectiveness", in the sense that they induce greater increases in resistance, present a greater degree of "incompatibility", which implies that the evaluation of the two concepts cannot be resolved with the same set of parameters and in a single reasoning. In simple terms, manifestations of incompatibility are the consequence of the differentiated behaviour of the consolidated layer and the underlying untreated substrate. They result from the combination of differences in the properties of the two adjacent elements (the treated layer and the untreated substrate) potentiated by the action of external acting agents. Differences in properties can be considered as ratios, while the action of external agents can be considered as multiplying factors. The weight to be given to each individual ratio and the value of the multiplier factors are issues that still await to be settled and validated with dedicated research work.

Testing to find the critical properties should be focused directly on the characterisation of the fully consolidated stone thickness and not on any partially treated specimen, since this last option would correspond to "averaging" the values of a certain consolidated zone and an untreated bulk substrate. If a particular treatment is capable of consolidating only the first 2 mm, it is exactly the properties of that 2 mm layer that matter and that should be looked for. The understanding of the overall behaviour of a consolidated stone will finally result from the integration of properties of the treated zone, the substrate, and the interface between them.

Obtaining the properties of such tiny layers is not straightforward for most consolidation products and the bibliography does not provide many examples on this kind of measurements. Certainly for this same reason, dealing with ratios of properties and assessing the incompatibility risk through reasoning with the role of individual properties or indicators are arguments not very popular in the literature ((Gauri, Gwinn, and Popli 1976), (Sasse and Snethlage 1996), (Delgado Rodrigues and Grossi 2007).

Examples of key-properties of the treated (TS) and untreated (US) stone are the elastic modulus of deformability (Young's modulus), strength (tensile, bending, or biaxial tensile), thermal expansion coefficient, hydric expansion coefficient, water vapour permeability, among others. Environment temperature (and its characteristic cycles) and humidity (as vapour or liquid) are the main acting factors. Context specific factors, such as the presence of clays as intrinsic components, the specific types of voids (fissures versus pores), the presence of salts, the presence of specific aerosols (such as SO_2) may be considered as synergistic factors and enter as such in a risk matrix.

Proper integration models need to be developed and validated, a methodology certainly at reach with the computational tools available to support these models. This is a hope and a certainty that authors sustain for the near future in the research on stone consolidation.

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The European TC 346/WG3 standards on the evaluation of conservation works

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SUMMARY: A specific European standardisation activity in the field of conservation of cultural heritage is essential to acquire a common unified scientific approach to the problems relevant to the preservation and conservation of the cultural property. The WG3 working group had been created with the aim of preparing standards to evaluate the products and methods used in conservation works. In particular it was aimed at producing standards relating to cleaning, consolidation and protection of porous inorganic materials. At present time a complete framework of standards dealing with cleaning and protection of cultural heritage objects has been published. Actually EN standards regarding consolidation works are still missing and the purpose of this paper is to stimulate the discussion on how to prepare specific standards according to the line proposed by the other ones already published for cleaning and protection treatments.

KEY-WORDS: surface protection, cleaning, water repellent, conservation works, consolidation treatments

1. INTRODUCTION

The conservation process of a cultural heritage object is developing through a series of operations, which can be summarized in the following scheme: 1) preliminary knowledge of the object and of the environmental conditions in which it is maintained; 2) direct intervention on the object; 3) assessment of the effects of the intervention itself; 4) monitoring of the intervention effects.

As regards item 2 it is therefore expected that products suitable for conservation are applied. These products are called to perform different functions, conceptually quite distinct. We can summarize them as follows (Amoroso & Fassina, 1983, Amoroso & Camaiti, 2006):

a) removal of unwanted materials, identified by preliminary investigations and by the conservation project;
b) consolidation of the constituting materials of the object under conservation. This term refers to operations on a micro structural scale, as well as those actions acting on a larger dimensional scale. The main purpose of consolidation actions is aiming at restoring cohesion within the object and to re-establish those characteristics of mechanical stability threatened by the deterioration processes;
c) re-instate of the missing parts, according to the forms and modalities established by the conservation project. This operation can include both strictly conservative purposes, and intentions aimed at making possible a more correct readability of the cultural and formal values of the object;
d) surface protection of the object against the main environmental deterioration agents, which negatively interact with the object during its life.

According to the above considerations it is evident that the products to be used in these four phases are manifold; e.g., these can be summarized as following: solvents, surfactants, surface consolidating agents, filling mortars, water-repellent protective agents. The methods of application of these products are also very important as well as those methods aimed at achieving one of the above objectives, not applying any product, such as cleaning using laser tools.

The professionals involved within the conservation project pose a series of questions: how the products are working? Will they achieve their goals? And to which level? In such a complex interaction, undesirable effects will also occur? And if so, to what extent? How long the products will retain their characteristics? When and why, they will begin to decay themselves?

Any professional and expert in the conservation field has been bothered by several questions, which are often difficult to answer. The questions are not new, and the preservation products come from a long history, in many cases as long as the history of the objects themselves, which, often very precious, were subject to maintenance since the time of their production.

The attempt to provide reliable, reproducible, precise answers is a question posed in recent times. It involves the different professionals who relate to each other in the field: first the project designer, in charge to choose the products and successively the restorer, who applies them using the best practices. The possibility of finding some suitable answers is strengthened by the involvement of experts in materials science who are familiar with conservation problems and can develop and apply appropriate studies to answer the posed questions. It is a matter of obtaining a series of measures before applying the products, repeating them after their application and making the necessary comparisons. The differences found are ascribed to the action of the products under investigation. A good example concerns the colour measurements recorded before and after the application of a protective product on a marble surface. If someone compares several products, the one producing the least colour change, will be chosen.

In these last decades a widespread scientific literature has been developed, both in laboratory and on field, concerning the assessment of many conservation products. At this point a crucial question should be considered: to what extent are the scientific data available in the bibliography comparable?

Hence raise the need to rely on shared and standardized testing protocols, which have the purpose of evaluating the effects of the products by standardizing the measurement procedures, making the data comparable to each other. The bibliography in the sector contains many proposals, as well (Alessandrini, 1995, 2008).

If otherwise the data were obtained with different methods, their comparison is limited and not very fruitful, and the comparison ineffective (Alessandrini & Pasetti, 1991, 2005).

The history of conservation products is largely yet to be written, although interesting reconstructions have been recently proposed. From this point of view, the history of the introduction of inorganic silicates is exemplary which, at the turn of the nineteenth and twentieth centuries, were compared from the point of view of their effectiveness, unwanted effects, therefore evaluating the potential damage that they could produce. Since then, some scholars complained that the evaluation was achieved through a mere visual comparison in the absence of standardized analytical protocol (Cattanei, 1993).

A scientific review of the large amount of data obtained during the twentieth century and in the first two decades of the present one would be of great help (Lewin, 1966). In fact, the standardization work is based on scientific research and it is mainly based on using correct and appropriate comparison methods; the drafting of the standards is carried out at national and international level; it derives from the scientific discussion and tries to satisfy the needs of rationalization and/or revision of the data, which are needed in this field of study. In this introduction the ongoing discussion and its historical roots was developed (Defus Agnieszka, 2020).

2. THE TERMINOLOGY ISSUE

In order to introduce the standards drafted over the last fifteen years, some terminological issues and basic definitions need to be specified[1],[2] in order to share with the reader, the concepts at the base of the standard documents discussed (Fassina, 2015). The considered conservation products have some common feature: they can be both natural and synthetic materials; very often they display polymeric molecular structure, which consists in a long chain of structural units, called monomers. The number of structural units could be 2, 3 (dimer, trimer) or around 5-15 units and, in this latter case, the term oligomer is used (Clayden et al., 2012, Callister et al., 2012).

When applied, the materials based on these products are fluid, in solution, in emulsion or in a complex chemical formulation; therefore, they have rheology properties on which the applicability of the product depends; to meet the final operating requirements, they undergo a setting and hardening process, which may be due to different mechanisms, including the most common polymerization and evaporation of the solvent. Once the setting and hardening process on the substrate is completed, the system (object plus treatment applied) acquires the final properties, and begins its service life period, on which the overall deterioration processes will occur (Biscontin & Driussi, 2003).

Based on the objects to be preserved and to the existing guidelines, the terms briefly introduced in the following assume slightly different meanings and characteristics. They are part of the conservation of

[1] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019) S. J. Chalk. https://doi.org/10.1351/goldbook.

[2] Joint Committee for Guides in Metrology (JCGM), *International Vocabulary of Metrology, Basic and General concepts and Associated Terms* (*VIM*), III ed., Pavillon de Breteuil: JCGM 200:2008, 2.2; 2001

porous inorganic materials, on which the standard discussed apply. However, please refer to the specific bibliography for further details.

Cleaning. This term indicates the removal of unwanted materials, identified by the analytical investigations and/or based on preliminary trials. Cleaning can be carried out by using aqueous systems (aqueous solutions with surfactants, chelants, etc.) or solvents, as well as mechanical or physical systems. Different systems are used in sequence or in combination with each other cleaning.

Surface consolidation. This term indicates a treatment applied by imbibition on a surface affected by deterioration phenomena such as pulverization or disintegration[3]. The treatment has the aim of restoring the lost cohesion, due to the deterioration processes acting on the substrate constituting materials. One of the predetermined effects concerns the re-establishment of the lost mechanical properties.

The surface consolidant is applied on the object external surface, but works by penetrating deeply, according to a concentration gradient, and appropriately settling and hardening into the material microstructure.

The action scale of a surface consolidant is extremely small and variable according to the porosity of the substrate on which it is applied and the consolidation mechanism itself, but it is often coincident with the molecular scale[4] (Siegesmund & Snethalage, 2014).

Adhesion. This term indicates the treatment according to which a detached fragment (or a new element identified by the conservation project) is placed in the expected position (Allen, 1984). The adhesive product is applied to the interface between the fragment and the detachment point. Relocation must take place on a precise geometrical basis and the interface must be clearly identifiable. It is also desirable that the adhesive forms a thin joint and that the adhesion forces are proportional to the object mechanical characteristics.

As previously mentioned, these general concepts are applied in a very different way depending on the object chemical composition (stone, plaster, ceramic, etc.).

Protective. With the publication of the Normal 20/85 document (Various authors, 1985), the distinction between the role of consolidation and of protection was established. In fact, before this publication Heaton (1921) and Warnes (1926) defined what the requirements needed for a "perfect stone preservative". From the 70s of the last century consolidation started to be considered as an operation aimed at restoring cohesion in depth, while protection is carried out through the surface application of chemicals; moreover, protective treatment is recommended whenever the most important deterioration factors act mainly on the external surface of the material (for example: action of pollutants, condensation of humidity, chemical-mechanical action of rains) (Amoroso & Fassina, 1983). In this paper we focus on the products that are able to impart water repellence properties to the surfaces on which they are applied. They are therefore hydrophobic substances, taking into account that in most deterioration mechanisms, especially those objects that are exposed to outdoor, liquid water has a fundamental role (EN 16851).

The main purpose of a water-repellent product is to reduce the transport phenomena of liquid water from the environment to the micro-porous matrix of an object. By limiting the liquid water ingress, the presence of any substances water-soluble is reduced and consequently the deterioration processes are strongly slowed down. This effect is obtained by changing the surface properties and in particular its wettability and capillary absorption capacity. In the meanwhile, the protective product shall not decrease importantly the water vapour permeability of the substrate. A correct balance in the properties of the final system, consisting of an object plus water repellent treatment, must therefore be optimized (Fassina & Mecchi, 2008).

It should also be taken into account, that some products perform several functions simultaneously; they are able, for example, both to restore the loss of cohesion and at the same time working to protect against the ingress of water.

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[3] Forms of alteration are defined by Normal UNI 11182: 2006 which is strictly related to natural and artificial stone materials. ICOMOS-ISCS, Illustrated glossary on stone deterioration patterns, https://www.icomos.org/publications/monuments_and_sites/15/pdf/Monuments_and_Sites_15_ISCS_Glossary_Stone.pdf ,

[4] Report and database on commercial consolidants and protective coatings. Progetto Nano cathedral retrieved on line: http://www.nanocathedral.eu/wp-content/uploads/2018/06/Nanocathedral-D1.2-Report-and-database-on-commercial-consolidants-and-protective-coatings-min.pdf

3. GENERAL REQUIREMENTS FOR CONSERVATION PRODUCTS

In the previous paragraph the expected requirements for products to be applied to cultural heritage object are mentioned. A general discussion on this issue will be presented in this paragraph. Generally speaking, the used products should be effective, but in the meanwhile, they shall not produce undesired changes (Alessandrini and Fassina, 2008). When a conservation work is designed it shall be taken into account that effectiveness shall not compromise the cultural value of the object.

Previously it was mentioned the specific issue related to the effectiveness of each conservation treatment, which is declined differently, according to the type of treatment. Considering the particular nature of heritage objects, it is possible to identify a series of general requirements that shall be respected by any type of treatment. These requirements are summarized in the following list; product shall: i) • not change the colour of the surface on which they are applied; ii) not change the surface gloss; iii) not release harmful by-products; iv) be durable while maintaining the properties they acquired during their service life; v) have adequate stability during storage.

By considering these observations it is clear that an overall comprehension of the performance of the product used for conservation purposes is a complex problem; hence it would be necessary to acquire a set of laboratory data and observations. The experiments should start from acquiring a series of information on the product itself, its composition and its properties, then continuing on laboratory models where the product is applied on a certain substrate prepared on purpose, and finally observing the results obtained in field case studies (Horie, 2010). In order to monitor product performance over time data collection should continue after conservation intervention.

In order to have a useful and practical approach, however, it is necessary to simplify the problem by modelling it from a theoretical point of view, addressing the data acquisition to a double evaluation: a) understanding the effectiveness of the product; b) understanding the potential harmfulness of the product.

Each of these two evaluations are based on the collection of information obtained from laboratory measurements and field observations. Only from an organized and critical collection of sufficient information, the conservation project reaches an overall assessment. Furthermore, it must be taken into account that the “perfect product” does not exist; on the contrary the study should take into account those products which, tested under the given conditions, provided the best performance on that specific substrate.

In conclusion the evaluation of the effectiveness and potential harmfulness of a conservation treatment can be obtained by observation and measurements carried out both in laboratory and in field.

Laboratory measurements can be carried out on heritage objects, samples or specimens from heritage objects, or on models of freshly quarrying or artificially aged materials. Field measurements are performed on heritage object surfaces.

4. THE STANDARDIZATION OVERVIEW

At the beginning of 2000 a detailed state-of-the-art examination of existing technical standard showed gaps and discrepancies. Many European countries use different procedures to design and evaluate conservation process for cultural heritage objects. A specific European standardisation activity in the field of conservation of cultural heritage was therefore essential to acquire a common unified scientific approach to the problems relevant to the preservation and conservation of the cultural property. It also ensures a synergy between professionals belonging to various scientific disciplines of the EU member countries.

Given these premises, the Business Plan BP presented by Italy aimed to harmonize the different conservation and restoration methodologies adopted by individual member countries. This need was linked to liberalization, introduced by the European Union in the restoration field, which would have allowed restorers and restoration companies from all over Europe to operate in everyone EU member countries.

In particular, the action proposed by Italy aimed to unify the methodologies, test methods and diagnostic

So initially the BP had foreseen five working groups that would develop a series of standard mainly focused on the following guidelines: 1) terminology; 2) characterization of the materials constituting cultural heritage and their deterioration products; 3) evaluation of the methods and products used in conservation works; 4) characterization of the microclimatic parameters that influence the alteration processes of the indoor and outdoor objects; 5) guidelines relating to the transport and packaging of works of art that are exhibited in temporary and permanent exhibitions.

The WG3 working group had been created with the aim of preparing standards to evaluate the products and methods used in conservation interventions. In particular it was aimed at producing standards relating to cleaning, consolidation and protection of porous inorganic materials.

Scope and fields of application of the most significant standard produced by WG3 will be discussed.

A general overview on the standards, such as the one proposed in this paper, acquire its complete meaning, considering this particular field in which we are called to evaluate the effects of conservation treatment.

Regarding the initial planned BP, that includes cleaning, consolidation and protection issues, at the present time, a complete framework of standards dealing with cleaning and protection has been published (Fassina 2007, 2008, 2014, 2015, 2020). Actually, consolidation EN standards are missing and the purpose of this paper is to stimulate the discussion on how to prepare them according to the line proposed by the other EN standards already published.

As already mentioned in the introductory paragraphs, any cleaning and protection intervention involve the use of methodologies and products, that shall be suitably tested to meet a series of requirements allowing the assessment of their effectiveness, harmfulness and durability. It is therefore important to set criteria for the assessment, step by step, of the products and methodologies performance, applied during the whole conservation process. These criteria shall be applied both for testing new products and for those already present on the market.

The lack of criteria for performance evaluations involves some problems:

a) difficulty of a full objective comparison between the performances obtainable with the use of the products currently on the market;
b) difficulty in developing a product application methodology or technology in each case study, which should be completely reproducible;
c) difficulty in being able to carry out an objective final test of the conservation work;
d) uncertainty in the drafting of the contract documents.

In analogy to most of the application sectors, which have reached far more advanced technological levels than those available to the conservation of cultural heritage sector, it is necessary to carry out performance evaluations using a set of tools and actions that are ascribed to the use of: i) significant parameters relating to the performance to be measured; ii) standardized and reproducible measurement methods of the various parameters; iii) limits of acceptability.

At first the working group was addressed to prepare standards related to the object surface protection which is the last step of the restoration/conservation process. This choice was motivated by the fact that in the various member countries for many years very similar tests were used for the evaluation of effectiveness. In Italy, since 1985, the Normal commission launched a systematic test program aimed at establishing both the requisites that a protective product shall fulfil and the criteria for evaluating its performance.

The following set of EN standards was produced (Figure 1):

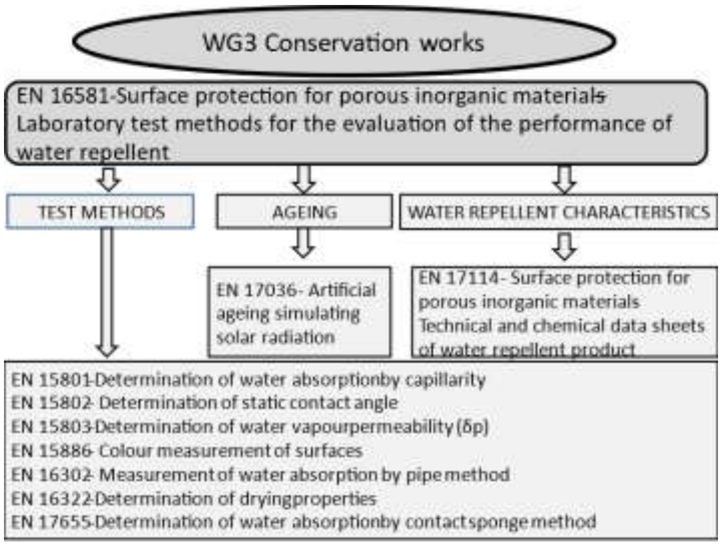


Figure 1. Complete set of standards to evaluate the performance of water repellent

a) a general framework document (EN 16581),
b) several test methods capable of characterizing the protective performance (EN 15801, 15802, 15803, 15886, 16302, 16322, 17655)
c) an aging test by using solar radiation wavelength (EN 17036)
d) a technical data sheet containing the chemical-physical characteristics of the protective product (EN 17114)

5. EVALUATION CRITERIA OF THE SURFACE PROTECTIONS APPLIED TO THE ARCHITECTURAL BUILDINGS AND SCULPTURES

Many mechanisms responsible for deterioration processes are ascribed to the presence of water and therefore the reduction of water absorption helps in slowing down the deterioration processes (Schaffer 1932, Fassina 1978, 1994, Fassina et al. 2002). For this purpose, the surface protection treatments, carried out to delay the deterioration processes are of particular importance in the conservation of the architectural heritage (Appolonia et al. 1993, 1995, Fassina & Mecchi 2008).

The EN 16581 standard concerns in particular on the porous inorganic materials "water-repellent treatments". The main objective of the water-repellent substances is in reducing of the penetration of liquid water and the soluble salts dissolved in it, by modifying the surface properties of the porous material. In fact, it is known that a water-repellent product, when applied to the surface of an object, causes a decrease in its surface tension, reducing the wettability of the surface itself (Fassina, 2015, 2019).

The depth of penetration of the water-repellent treatment depends on the capillary properties of the substrate and of the water repellent product as well as on the methodology and duration of the application.

A water repellent shall meet the following requirements: a) minimize the absorption of liquid water in the substrate (Figure 2a); b) minimize the reduction of substrate water vapor permeability (Figure 2b); c) minimize the colour variations of the substrate; d) avoid producing harmful by-products after application; e) maintain its physical and chemical stability.

The water-repellent products shall be applied on the surface of the heritage object only after having been tested in the laboratory on representative samples of the same material constituting the object.

The standard for the evaluation of water-repellent treatments is based on the measurement, by using standardized test methods, of appropriate parameters capable of assessing the characteristics of the product applied on each substrate.

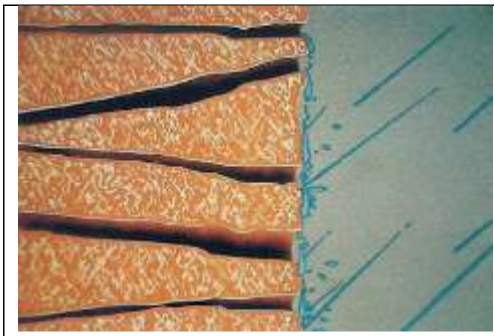


Figure 2a. Water repellent behaviour of an effective compound

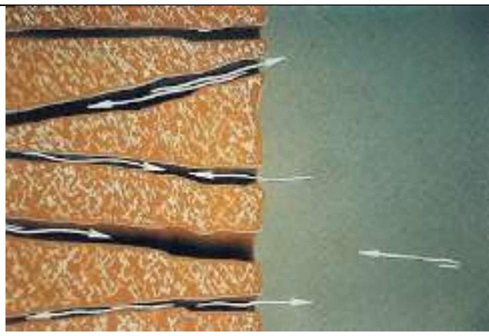


Figure 2b. Water vapour permeability behaviour of a safe compound

The application of the products on site can be carried out by brush, spray, capillary migration by means of compress or immersion in the case of small mobile objects.

In laboratory the application of the water repellent on specimens is carried out by capillarity because, in doing so, the reproducibility conditions are guaranteed.

If the product to be tested is not applicable according to the capillary migration method (for example when using an emulsion product), the application method used must be described in detail in the test report.

The technical data sheets shall report all information relating to the chemical nature of the active substances, the solvent in which they are dissolved and their concentrations. In order to evaluate the performance and durability of the water-repellent product applied to the substrate, aging tests reproducing similar environmental conditions to those surrounding the object, shall be considered.

The evaluation of the performance of water-repellent products carried out in laboratory is based on the measurement of various parameters and by using standard test methods, before and after aging.

Satisfactory laboratory results obtained cannot be automatically extended to any field situation.

The particular environmental context in which the heritage object is located and the other factors that determine the condition, such as its exposure to atmospheric agents, the content of soluble salts and problems related to the penetration of water often require further investigation.

Particular attention shall be paid to the choice of the chemical-physical characteristics that are fundamental for the evaluation of the products to be used for protective surface treatments purposes. The basic characteristics are as follows:

- ability to limit water absorption;
- transfer of hydrophobic properties to the material surface;
- ability to let the water present within the substrate to escape as water vapour;
- maintenance of colour values

To evaluate the ability to limit water absorption. Three different types of tests have been proposed.

EN 15801:2010-Determination of water absorption by capillarity

EN 16302:2013-Measurement of water absorption by pipe

EN 17655:2022-Determination of water absorption by contact sponge method

Conservation treatments of stone materials in architectural buildings and sculptures often change the impact of water transport from the external environment into the porous substrate of the objects. It is therefore very important to study the absorption phenomena (Fassina 2015, 2016, 2019).

A first general method allows to determine the absorption of water by capillarity by the porous substrate, through the contact of a specimen with a pack of filter papers, soaked with water (EN 15801). The measurement consists in the determination of the specimen weight at defined time intervals; a curve is then drawn, which relates the amount of absorbed water as a function of time. The different parameters obtained allow to verify, for example, how a protective treatment decreases the water absorption capacity in the micro-porous matrix of a stone (Figs 3, 4).

A second method allows to carry out absorption measurements by means of the so-called *contact sponge method*, that is a method using a sponge soaked in water and placed in contact with the surface under examination (EN 17655). The method focuses on phenomena, which includes a quick absorption of water, within a short interval (60s/120s), by the surface of a substrate. The different times are chosen according to the compactness of the substrate on which the measurement is made.

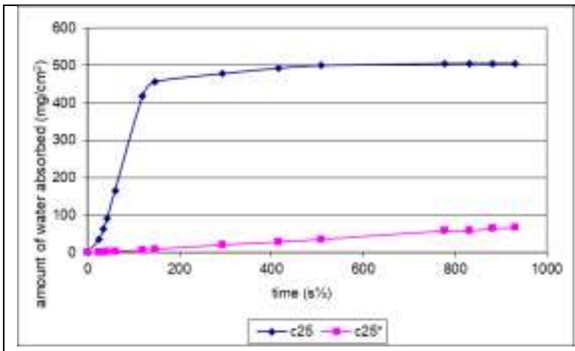


Fig. 3. Water absorption curve (rhombus and square lines are respectively before and after the protective application). After treatment a significant water absorption reduction is observed.

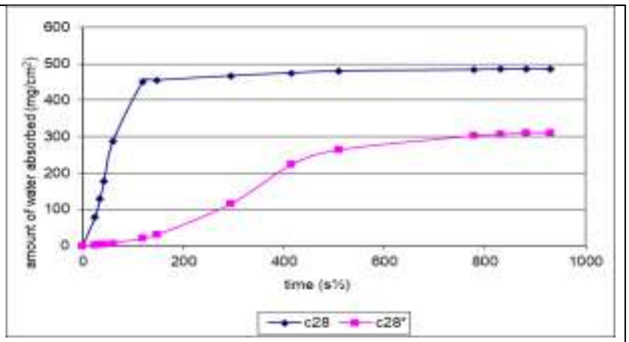


Fig. 4. Water absorption (rhombus and square lines are respectively before and after the protective application). Less effective protection by another protective product showing a partial reduction of water absorption

For this purpose, natural sponges in cellulose fibres are used, placed in special plastic contact containers. The thickness of the sponges is such as to exceed the edges of the container. The sponge is uniformly moistened, using a syringe, with a known quantity of deionized water, and the container pressed manually in contact with the surface until it touches the edges, for the given time. The pressure exerted on the sponge is determined by the contact of the edges of the container with the surface under examination and is kept constant during the test time. The weight of the container with the embedded sponge is measured before and after contact with the surface, and the difference in weight provides the amount of water absorbed by capillarity from the surface, during each measurement (Figs 5, 6).

Fig. 5. Contact sponge inside plastic bag with the syringe

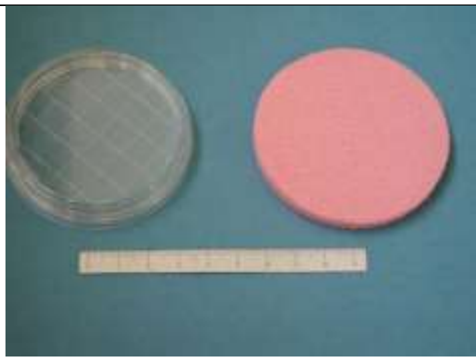


Fig. 6. Contact sponge and the plastic container

There is also the possibility of carrying out a measurement of water absorption with the pipe method (EN 16302) (figs. 7, 8), which makes the measurement more general than the so-called Karsten tube, which had been developed as a recommendation by the RILEM group[5]. It is a matter of keeping in place on the surface of the material under test, a device made of glass or plastic material, which consists of a cell and a graduated pipette. The cell, filled with water, is placed on the surface with a sealed contact and therefore the graduated pipette measures the quantity of water absorbed.

The latter two methods have the advantage of being able to be applied both in laboratory and in situ, thus allowing an application of the standard on site.

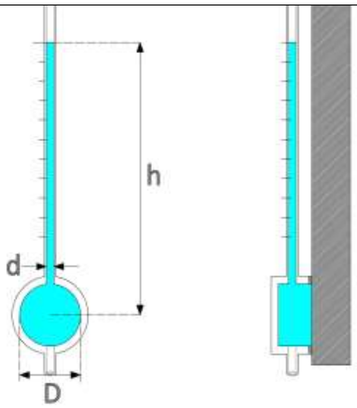


Fig. 7. EN 16302. Scheme of pipe type for vertical surfaces. (from EN 16302)

Fig. 8. Cell, graduated pipette and water supply used for EN 16302.

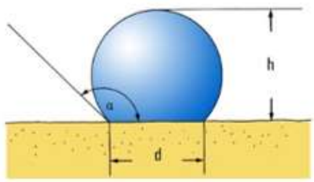
EN 15802:2010 DETERMINATION OF THE STATIC CONTACT ANGLE

This standard specifies a method for measuring the static contact angle of a drop of water deposited on the surface of a specimen. The measurement takes place through an illuminator and a viewer that allows to observe the drop slightly enlarged, from which the geometric parameters needed to determine the contact angle are measured. It is necessary to acquire a sufficient number of measurements for the determined values to have a statistical meaning (e.g., 25 on a surface 5x5 cm). The standard can be applied to materials both untreated and subjected to any treatment or aging (Figs. 9, 10).

5 RILEM, *Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages*

EN 15803: 2010 Determination of water vapor permeability

The standard specifies a method for determining the water vapor permeability (WVP) of porous inorganic materials specimens. The method uses a sealed measuring cell closed by a specimen of stone material; on the bottom of the cell a known quantity of water is placed (Fassina 2019). Evaporation saturates the gap between liquid water and the specimen; over time the vapor permeates through the substrate. Thin specimens (1 cm thick) are usually used in order to weight the amount of water lost by the system at defined intervals. Also, in this case, a curve relating the quantity of water flowing through the specimen as a function of time is reported. Figure 11 shows the comparison of the flow variation on individual samples before and after treatment.

	
Fig. 9. Apparatus for the measurement of contact angle	Fig. 10. Contac angle α of a water drop

The measurement is quite long and takes about ten days. The standard can be applied to materials both untreated and subjected to any treatment or aging. As it is evident an appropriate assessment of the performance of a protective substance, concerning each case study, can be obtained through a systematic collection of measurements of different parameters; each of them is describing the impact of water movement in liquid or vapour form (EN 16581).

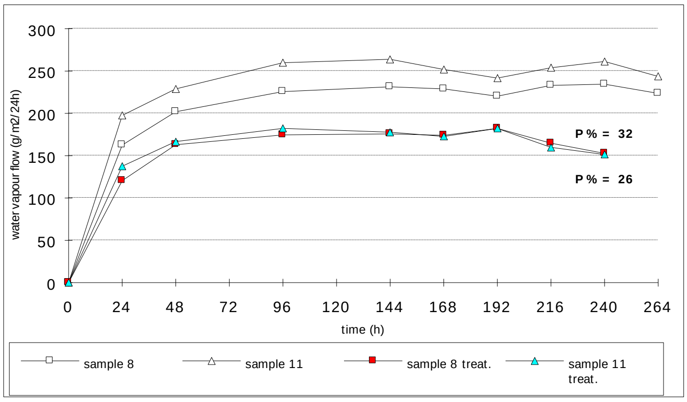


Figure 11. Comparison of the water amount passing through the specimen before and after the treatment

EN 16322:2013 - Determination of drying properties

The drying test provides information on the transport properties for both phases: liquid and vapor. Since it includes both transport in saturation conditions and in the vapor phase alone, it constitutes a link between the two tests previously described (EN 15801 and EN 15803) and is very important for the thermo-hygrometric characterization of the material. Since it is strongly dependent on the boundary conditions, the latter must be well defined.

In general, the drying process involves a three-dimensional transport of heat and humidity. The drying behaviour of porous materials depends on the:

- properties of the material (stationery and transport of humidity)
- climatic conditions (temperature and relative humidity)
- conditions of heat and vapor transfer (air velocity and surface roughness).

The properties of the material affect the speed and amount of moisture that is carried within the material. The boundary conditions, i.e., the combination of climatic and transport conditions define both the speed and the amount of moisture that is transferred to the surrounding atmosphere.

The drying properties of materials can be calculated from a curve indicating the weight loss of the water mass within the sample, as a function of time, during a drying experiment. Two significant phases can be observed:

a) the first is characterized by the transport of liquid water to the surface followed by evaporation and the weight loss is almost linear. The surface remains moist allowing evaporation at a constant rate, as the water moves to the surface fast enough to compensate for the losses due to evaporation. Surface evaporation is largely determined by the boundary conditions, i.e., temperature, relative humidity and air flow rate. The steepness of the drying curve during the first stage therefore reflects these conditions.
b) the second drying phase begins when the amount of water brought to the surface becomes too small to keep it wet and the evaporation rate decreases. The transport of liquid water is replaced by the vapor diffusion process and in this case the properties of the porous material play a fundamental role.

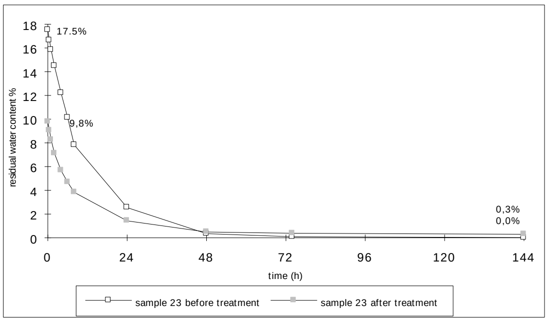


Fig. 12. Evaporation curve: empty square untreated, full square treated. The untreated specimen shows a slower evaporation rate.

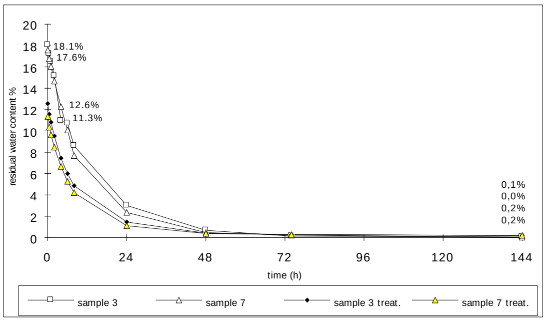


Fig. 13. Evaporation curve: empty square untreated, full square treated.

EN 15886: 2010 - Measurement of the colour of the surfaces

The measurement of the surfaces colorimetric parameters is carried out by using a reflectance colorimeter, which records colour measurements of a circular shaped surface and generally of 8 mm diameter; it is possible to acquire the measurements in two different ways, normally chosen according to their surface gloss: including (SCI) or excluding (SCE) the specular component. The measurement takes place with an illuminant D65. It is a theoretical visible light source with a spectral distribution potential; in particular the illuminants D represent the phases of daylight.

The colorimetric parameters are acquired in a coordinate system called CIE L * a * b *, (CIE Commission Internationale de l'Éclairage) designed to approximate the perception of colour according to human vision through a numerical determination of colour. The L * parameter expresses the brightness, the a * and b * parameters represent the coordinates of the colour point on a Cartesian plane, respectively the green-red coordinate (a *) and the yellow-blue coordinate (b *). The acquired data are subsequently processed in order to evaluate the changes in brightness (ΔL *) and colour (Δa * and Δb *), for example before and after a conservation treatment, as well as the global variations of the chromatic parameters (ΔE *), expressed by the Euclidean distance of two points in a three-dimensional colour space:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$

For each investigated area, a sufficient number of colorimetric measurements are carried out according to the chromatic homogeneity of the sample, in order to obtain a statistical basis for the measurement; generally, the number of measurements varies from 5 to 25. In order to evaluate a conservation treatment, the same number of measures is carried out before and after the treatment in the same points.

Aging methods

Conservation products are applied to materials, which are often centuries old. The conservative history of monuments leads us to consider the most different and extreme conservation environments. The standardization also takes this aspect into consideration and specifies how the products or the system formed by material and the applied product, can be studied over time, during an accelerated aging cycle (Feller 1994). In this case too, the standardization is the result of a wide amount of researches reported in bibliography. In this regard, the titles of the standards drawn up in order to indicate accelerated aging methods are mentioned:

EN 17036: 2018 Artificial aging by simulated solar radiation of the surface of treated and untreated porous inorganic materials

The standard determines the long-term susceptibility of treatments used in the conservation of porous inorganic materials, when they are exposed to solar radiation. Some examples may concern materials that underwent a treatment during a conservation intervention (e.g. cleaning, surface consolidation, water-repellent protection, biocide treatment) or materials that may underwent a chromatic variation following exposure (e.g. mortars and some natural stones): the procedure can be used to evaluate the treatment effects soon after the application and over time in relation to untreated or unexposed material specimens.

6. SURFACE CLEANING (EN 17138, EN 16572, EN 17488)

Cleaning is an important operation in the conservation plan and generally is carried out before consolidation and protection of deteriorated materials (Amoroso and Fassina 1983).

Cleaning has the aim of removing unwanted materials, which negatively affect the conservation of the object and/or which limit its correct readability. The materials to be removed may derive from new formation processes (efflorescence, black crusts etc.), from deposit phenomena (deposit of atmospheric particulate), from intentional or non-intentional additions (residues of non-functional products, repainting, stains, etc.). Materials to be removed may be formed on the surface of the object or imply a more complex distribution even within the substrate; they can be unstable over time and as such shall be removed to avoid further damage.

From previous considerations the primary purpose of cleaning is the removal of both the surface layers and the alteration material, which penetrated within the porous substrate and moreover:

- constitute a current or future danger for the object conservation,
- disfigure the object hindering correct readability,
- represent a non-original addition incompatible with the history of the object.

It is widely demonstrated, by the researches of many authors, carried out over the past fifty years, that the formation of black crusts constitutes a source of continuous decay due to the instability of the deterioration products, which, containing soluble salts, can be dissolved in moisture present in the atmosphere in wetting conditions and subsequently, in the drying phase, they are subject to crystallization, which induces mechanical stresses inside the porous material.

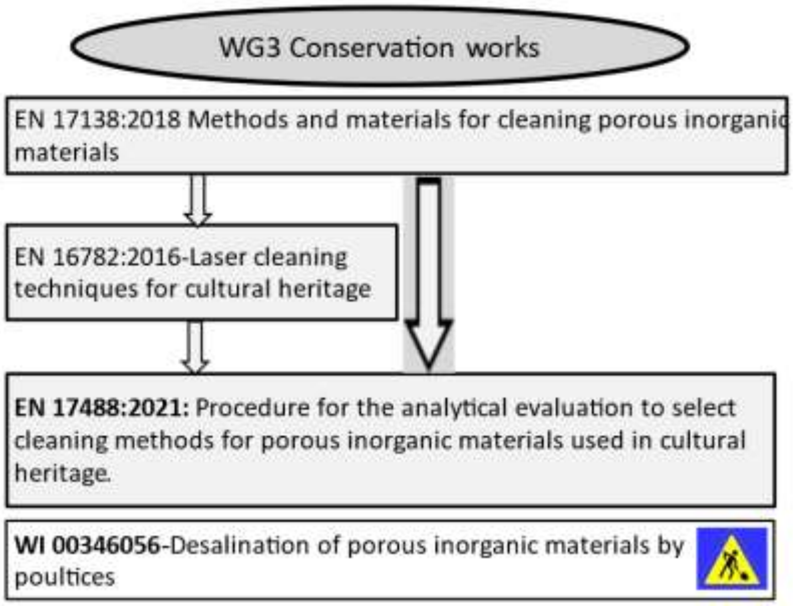


Figure 14. Complete set of standards for evaluating and choosing the products and methods to be used for cleaning the heritage object surfaces.

Given these premises, it was necessary to provide to restorers a standard containing the guidelines for choosing the most suitable systems for cleaning historical-artistic artefacts as well as architectural decorations of heritage buildings. Furthermore, the standard is useful for those responsible for the conservation projects of architectural, archaeological and historical-artistic heritage. Regarding this issue the standards reported in fig. 14 were prepared and published.

EN 17138: 2019 Methods and materials for cleaning porous inorganic materials

This standard represents an operational reference for those involved in the conservation of tangible cultural heritage, including the competent ministries and bodies responsible for the protection of cultural heritage, as well as for all conservation professionals (architects, conservators/restorers, conservation scientists, curators, etc.)

As cleaning produces irreversible effects on the object it shall be carried out with the necessary caution, in order to prevent any irreversible damage to the object itself. Furthermore, inadequate or inappropriate intervention can speed up deterioration processes or can eliminate surface layers, which are not documented or that would allow a better understanding of the history of the object (Fassina 2019).

The document describes the methodologies and requirements for cleaning methods applicable to natural stone, ceramic, plaster, mortar and concrete. Some methods described in this document cannot be applied to materials sensitive to the action of the products or systems used. For example, some lithotypes, wall paintings or other types of decoration may contain sensitive components, which can deteriorate as a consequence of the use of inappropriate cleaning system. In this concern, for each method described, recommendations regarding the applicability of the various types of materials and any damage to specific types are provided.

The useful requirements for choosing the most suitable type to be applied to individual objects are indicated. In particular, the importance of some general requirements such as selectivity, efficacy and controllability is underlined. Preliminary investigations including both the identification of the substrate nature and of the unwanted materials to be removed are recommended. In addition, to assess the effectiveness and potential damage (harmfulness) some trials on predetermined areas should be carried out. This evaluation should be continued during the cleaning operations and subsequently at the end of the restoration work by performing periodic monitoring. After illustrating all the preliminary stages and the necessary requirements, the document describes the cleaning methods divided into: systems using water, mechanical systems, chemical cleaning and physical systems.

Cleaning with aqueous systems includes the use of nebulized water, water spray, water applied with injection-extraction systems, steam, applications of compresses consisting of absorbent material. All the methods described for water cleaning are based on the principle of the solvent action exerted by water, while the various methods of application highlight a different removal effectiveness. For example, the spray system allows to use the minimum amount of water and, at the same time, to have a greater contact surface between the cleaning agent and the surface that must be cleaned. With this method, the cleaning action is exclusively based on the water solvent action avoiding any mechanical action, which instead occurs when the surface is treated with a jet of spray water. Injection-extraction and steam methods can be used in special cases. Finally, the methods which use aqueous compresses act through physical contact and depending on the support medium (cellulose pulp, gel, clays), minimize the release of water-based solutions into porous materials. In general, the most used methods are those with nebulisation, which are very effective in removing dirt on compact materials, but which shall be used with caution on very porous materials.

Mechanical systems use the abrasive action of a powder which is projected, under pressure, onto the surface to be cleaned. The effectiveness of removing dirt depends on the hardness of the abrasive material, the pressure of the jet, the diameter of the hole through which powder is ejected, the working distance, the size and shape of the powder particles. It is a poorly selective method as it progressively removes both the unwanted material and the substrate to be preserved and it is therefore mainly based on the operator's skill.

The document does not recommend mechanical methods which, due to their aggressive action, are potentially harmful on most of the surfaces considered.

Finally, in some special cases, "peeling systems" can be used which consist in the application of film-forming products applied in the liquid phase and which subsequently solidify by drying. When the film is removed the dirt is detached from the surface.

Cleaning with chemical agents varies through a wide range, given the considerable availability of chemicals offered by the market and which can act as solvents, chelators or surfactants. For example, cleaning with organic solvents can be used if natural or synthetic materials must be removed, such as organic macromolecules deriving from treatments with natural substances, such as terpenic resins, or with synthetic polymers such as vinyl, acrylic or silicone resins.

The use of highly acidic or alkaline substances is prohibited even if in the past numerous applications was carried out. Slightly alkaline or acidic substances in a pH range between 5.5 and 8.0 can be used. In this regard, ammonium carbonate and bicarbonate can be used, taking care to ensure that pigments containing copper, such as azurite, malachite, verdigris, are not present (Fig. 15).

Fig. 15. Cleaning test area with ammonium carbonate

The compounds included in the category of chelators can be effectively used for the removal of black crusts, iron stains, calcium oxalate-based films.

Ion exchange resins are used for the removal of thin deposits of gypsum, calcium carbonate or protein materials deriving from treatments with natural substances.

Finally, bio-cleaning has recently been introduced, which uses living and non-pathogenic microorganisms to remove sulphates, nitrates and organic material.

Physical systems include laser cleaning which was the subject of a separate standard (EN 16782).

EN 16782: 2017 Cleaning of porous inorganic materials - Laser cleaning techniques for cultural heritage

The numerous cleaning methods experimented the use of laser-based techniques, introduced during the 90s of the XX century, seemed particularly promising as they minimize the production of dust and residues, and do not need, water. However, in the current state of technology, even laser methods can give rise to harmful problems for the product, especially if applied by not well-trained staff; also, the necessary equipment sometimes appears to be poorly manageable and of rather high cost.

Despite the large amount of systematic and multidisciplinary investigations on the laser cleaning technique, the natural suspicions had not been completely overcome, nor the operational areas clearly defined.

The cooperation of physicists who have studied the laser-material interaction processes and designed the dedicated laser systems, of chemists and petrographers who have carried out accurate analytical investigations, of archaeologists, art historians and restorers who have assessed the historical-artistic readability and the effectiveness of the technique, as well as, finally, from companies that have engineered the prototypes, it was possible to provide many indications and guidelines on the use of laser cleaning for the restoration of stone surfaces, metal artefacts and paintings (Sabatini 2001).

Although in recent decades studies on the application of lasers to the cleaning of artistic and architectural artefacts have intensified, there were however critical issues. In order to clarify which parameters should be known when dealing with such a type of cleaning a EN standard was prepared. According to this standard, laser cleaning consists in the removal of unwanted surface materials from a substrate using laser radiation. Removal occurs through photo-thermal and / or photomechanical and / or photochemical processes (Sansonetti 2019).

Laser ablation causes the removal of materials in the form of molecular radicals, vapours or dusts and it is caused by physical phenomena due to the selective absorption of radiation by the material to be removed.

Laser cleaning is generally characterized by high precision and selectivity, which can allow stopping at a pre-established level, preventing any damage to surfaces. As with other cleaning systems, laser cleaning should only be performed by trained operators with sufficient knowledge of all laser safety regulations and guidelines.

The standard is focused on defining the requirements for the selection of laser cleaning methods and devices applicable to the cleaning of stone, ceramic, plaster and stucco products. Laser cleaning should not be used when safe working parameters cannot be identified.

The standard also provides guidelines for choosing the operating parameters of the laser, in order to optimize the cleaning procedure. Two categories are considered:

a) Laser Q-switch and Long Q-switch, providing pulsed radiation in the range from a few ns to a few tens of µs, allowing the emission of pulses with extremely high peak power;
b) Free running laser with a pulse duration in the range of µs-ms.

Among the parameters to be taken into consideration we mention

- the fluence, i.e., the energy supplied per unit of surface,

- the repetition rate, i.e, the number of pulses per second,

It is important to identify the working fluence, which is the energy density range in which photo-ablation occurs without causing damage to the substrate. This test is generally carried out in situ without the need to take samples by varying the laser energy and therefore the fluence until a visible damage on the irradiated surface is observed (fig. 16).

Figure. 16. The red laser pointer indicating the area on which the laser radiation will hit.

Figure 17. During cleaning traces of azurite were discovered under the grey-black deposit of carbonaceous particulate pollutants.

EN 17488- Procedure for the analytical evaluation and selection of cleaning methods for porous inorganic materials used in cultural heritage

The standard was recently published in 2021. The purpose of the standard is to provide a series of procedures aimed at assessing the harmfulness and effectiveness of a cleaning method to be applied to all surface materials. and statuary, including layers of paint as a finish. The assessment is based both on the use of non-invasive on-site techniques and on the collection of samples to be studied in laboratory. Harmfulness assessment takes priority over effectiveness.

The document aims to provide a shared methodology in order to select the most appropriate method for the surfaces present in a conservation project and to optimize its parameters. The document applies to:

a) all cleaning methods, characterised by parameterization and reproducibility (EN 17138). Part A;
b) all new methods under development. Part B.
c) Since the cleaning is aimed at removing material of natural or artificial origin, which can potentially damage the substrate or which may limit its correct readability, it requires extreme caution and the need to minimize risks (fig. 17).

An effective cleaning strategy requires careful consideration of certain aspects such as the context and sensitivity of the object to be evaluated (for example the presence of gilded polychrome surfaces or extremely delicate materials such as those made of plaster) and its conservation conditions, which can lead to a lowering of the damage risk threshold during testing.

Therefore, it shall be taken into account that the cleaning method adopted may involve undesired variations in the substrate to be preserved (for example inherent porosity and surface roughness), the release of residual substances and the formation of stains, which are not compatible with the material and which could interfere with future conservation interventions.

A protocol of analytical tests is planned; it can be applied to the various cleaning methods tested in order to evaluate the extent of possible damages.

The assessment of the effectiveness and potential harmfulness of the cleaning methods shall be carried out on site by establishing a "trial area" as a preliminary phase before starting any intervention.

The document identifies the analysis and observation systems with which cleaning methods can be selected and assessed as part of conservation interventions.

The initial assessment for a building or similar immovable object will take place on site with non-invasive systems. If necessary, it can be followed by appropriate micro-invasive or invasive laboratory analyses.

Each method requires different considerations to select the most appropriate investigations.

The assessment of harmfulness for chemical cleaning methods requires a specific set of investigations on the possible interactions between the chemicals and the products to be removed, in particular the formation of by-products that could be harmful to the substrate.

Consequently, the procedure for chemical cleaning will follow a different path (fig. 18). For details of the analytical procedures see standard EN 17488.

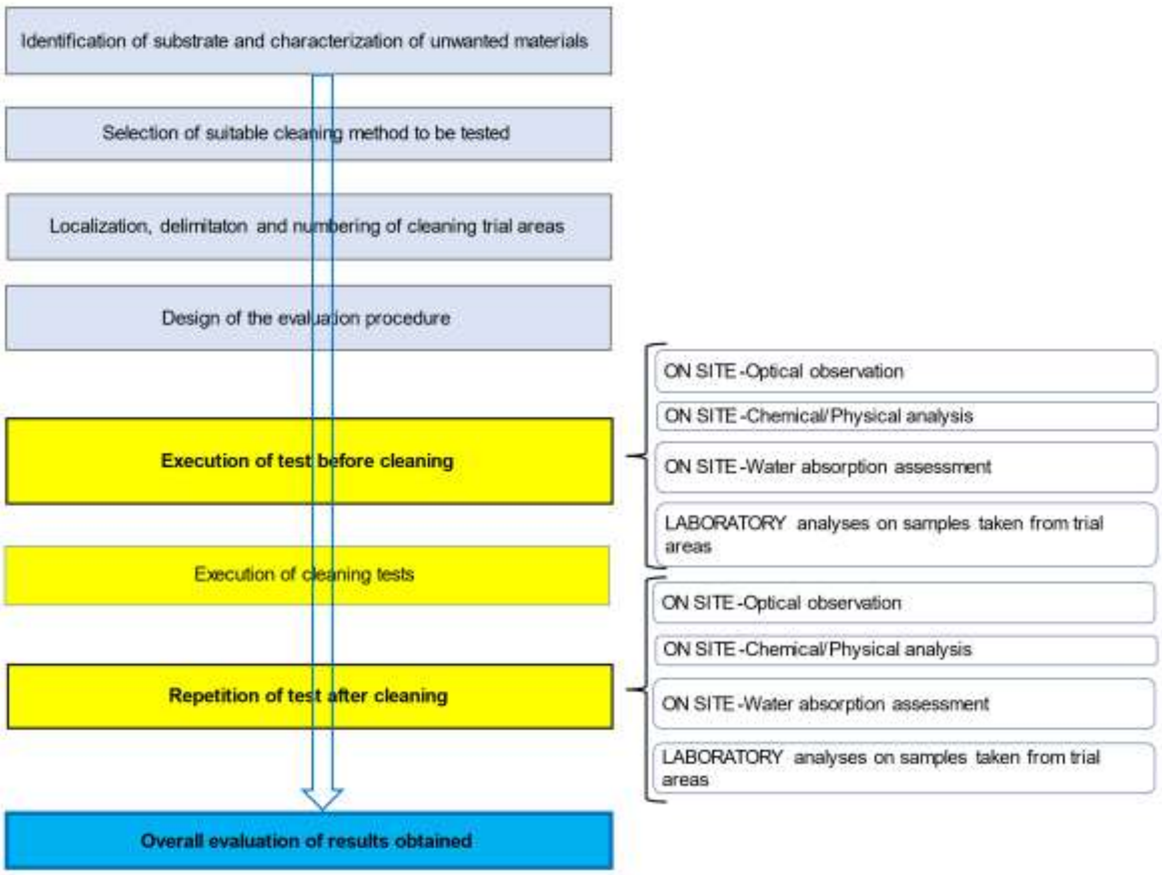


Fig. 18. Flow chart of the procedure for cleaning evaluation (from EN 17488)

7. CURRENT PERSPECTIVES IN EVALUATION OF CONSOLIDANTS

The use of consolidants treatments on stone materials, both natural and artificial (such as plaster ceramic and stuccoworks), is aimed at give back the set of cohesion forces into the material bulk and on its outer surface, whose loss is due to weathering. It is of crucial importance to evaluate the effectiveness of a treatment in the specific case, where the product features are influenced by the stone substrate, the environmental condition, the skill of the operator. For these reasons several testing protocols have been proposed recently in the scientific literature on Heritage (Becerra 2019). Nevertheless, CEN TC 346 or other standardization bodies are still in the run of methodological processing, and the sharing of a standard protocol is still missing. On the contrary a general document on the evaluation of protective treatments was published in 2015 (EN 16581), as before mentioned.

The scientific community agrees on the list of requirements to be achieved by a consolidant treatment:

- effectiveness in recovering correct cohesion forces to the stone material at a molecular level;
- increasing of mechanical strength;
- good penetration in the bulk of the material;
- maintenance of optical properties of colour parameters and gloss;
- maintenance of similar water transport mechanisms respect to the untreated stone material;
- good chemical compatibility;
- avoiding of any dangerous by product, even during the setting and/or the decay of the product;
- durability (resistance to different decay agents) (Amoroso & Fassina, 1983; Doehne & Price, 2010; Snethlage & Siegesmund, 2014).

Most of the testing methods in use and the results already published have been carried out and designed in order to test organic products. Since several years and currently the most innovative products which get an interest in the research projects are based on an inorganic composition. In fact, ammonium oxalate, diammonium phosphate, nano-lime, nano-silica are among the most studied products. This approach implies that very often the testing protocol should be designed taking into account the specificity of the product to be tested. As an example, working with phosphates implies that the measure of the distribution and the degree of penetration could be studied working in order to map phosphorous phases.

The scientific community concerned about this kind of problem face a double stepping: testing from lab specimen to real case architecture, and from laboratory analytical methods to portable instruments.

On real objects the most appropriate practice requires the best products should be chosen in relation to the specific features of the stones (chemical and mineralogical composition, porosity value and its distribution, decay pattern), features of the site (relative humidity, temperature), application methodology.

Generally speaking, most of the research currently on the run is aimed at working with portable non-destructive techniques. Here following we briefly overview the contribute of the most diffused techniques used in recent literature.

Drilling Resistance Measuring System DRMS. Test consists in drilling a hole at a defined constant revolution speed x (rpm) and constant penetration rate v (mm/min) and measuring the penetration force needed in function of depth (Ferreira Pinto, 2012). The main advantage of the DRMS regards its specificity in assessment of in-depth consolidation effect. Unfortunately, it has some drawbacks due to the so called "chisel edge effect"; Generally speaking, the DRMS seems to implies some drawbacks both on soft stone materials and on very abrasive ones such as quartzite even if some sandstone with quartz/silicatic component could give the same drawback regarding the possible abrasive effect on the drill itself. Mimoso and Costa (Mimoso & Costa, 2006) proposed a variation in producing the hole which enhanced the quality of data obtained. The quality of data comparison should be enhanced by the possibility to get drilling data from a sound stone, the untreated decayed stone, and the treated one. This comparison is not easy to be obtained. Quite often there are problems in considering the value of the outer mm of the treated stone, especially if the consolidants product affected only that area. The problem seems to regard the effect confined in the outer surface which implies a problem in interpreting the data coming from the underneath bulk. It is a semi-destructive method, but the holes obtained are small enough to be possible on a very large architectural surface.

Peeling Test. The Scotch tape peeling test could be performed using an adhesive tape with known resistance to tensile load and adhesion capability, as specified in ASTM D-3759 and ASTM D-3330. These standards are not yet accepted in cultural heritage community; the test allows a semi-quantitative evaluation of consolidation treatment and recently proved to be effective and quite reproducible (Defus, 2021). the test is mainly based on a weight measure of a calibrated strip of tape pressed gently and then removed by a decayed surface; this procedure is carried out before and after the consolidation treatment. After the consolidation the micro particles lost by the action of the tape should be less in weight and in number. Recently the test has been implemented by an image analysis of the tapes, immediately after the removal from the stone specimen, in order to obtain a numerical value indicating the difference in pixels occupied by particles before and after the treatment procedure (Defus et al, 2021; Drdácký et al. 2015).

Portable NMR. NMR proved to be fruitful in studying the structures of porous media basing on the measurement of relaxation times and diffusion coefficients of water introduced into the porous system. Several scientific papers dealing on water-saturated rocks have shown that relaxation time distributions are close to pore size distributions as measured by other techniques such as Mercury Intrusion Porosimetry. A great improvement was made possible by the Unilateral NMR probes. (Capitani et al. 2012).

When a stone is treated with a consolidants product, the variation occurring in its pore size distribution and the depth of penetration of a treatment inside a stone, are all important and critical tasks to be assessed, where NMR plays a major role, as this technique provides a powerful non-invasive tool for investigating such features in porous materials. The technique proved to be useful in order to study the difference between a specimen treated and a not treated one, because the technique allows studying the distribution of water in a very precise and sensitive manner.

Ultra-close-range photogrammetry. It is based on the same principles of classical photogrammetry, but it is applied at a micro scale; it has been used to provide a measurable 3D model of a very small area, by means of digital images. The technique is non-invasive, being a non-contact method, and one possible application regards the assessment of the effect of a consolidation product directly on-site.

Photogrammetry is often used in Cultural Heritage to study the state of conservation of an object, providing easily measurable models, and allowing to highlight dimensional variations occurring during conservation treatments; the ultra-close-range photogrammetry allows to corroborate other semi-invasive techniques such as for example peeling test, assessing the surface morphology and its variation in consequence of a consolidation treatment (Manganelli del Fà, 2015). The system proved to be easy to be applied and effective, portable and simple.

Portable ultrasound equipment. The test is rapid, non-invasive and economic; the critical point is in assuring a good contact between the probe and the surface, especially when this latter is rough. At the moment several different gels are under testing in order to improve this aspect. Unfortunately, some of the gels impart undesired features to the stone surface where they have been applied. If operated with a gel provided by most of the producers, the testing method could have some problems: in fact, these gels are silicone-based and the gel itself implies that no other test could be carried out on the same surface "soiled" by silicone. Some other tests have been carried out with gel composed on a polysaccharide base. A second point regards the geometry of the test. Transmission obtained good results in recent not yet published testing at ISPC labs. Transmission on site could be carried out only on specific architectural elements which allow the possibility, such as for example columns (with a limited thickness) or angular slabs or other types of elements

X Ray Computed Tomography is one of the most powerful non-destructive techniques for the whole volume inspection of an object giving morphological and physical information on the inner structure of the investigated samples. It is possible to perform high resolution micro tomography of objects with voxels size of a few microns.

*The μ-Computed T*omography studies utilizes conventional X-rays, even if using synchrotron radiation (SR) source, several advantages are provided: quicker acquisition time, better sensitivity and contrast, higher voxel size resolution. The synchrotron radiation X-ray micro-computed tomography (SR-μCT) it could be considered a very powerful technique in studying the effects induced by inorganic consolidant treatments on the stone microstructure; in fact, the solutions ingress by capillarity the pore network, fill the voids and change the 3D pore system at the micro-scale. (Possenti et al, 2019)

8. CONCLUSIONS

Anyone who carries out a conservation intervention faces the main aim to check the results obtained, as well as the quality of the interventions. The same spirit moves those who are called to approve a project or to judge the results obtained by restorers, taking into account the fundamental principles of conservation. Very often, however, we limit ourselves to a visual observation, a subjective evaluation or the outcome of incomplete trials. There is therefore a long walk-in building operators' awareness regarding the need for shared test protocols, making scientifically sound the possible results comparison. Many problems are still open in the field, also with the aim of improving the available test protocols, especially as regards surface consolidation.

We also feel the need to disclose a general framework of concepts and ideas which are fundamental in the discussion on standardization, in order to strengthen the application of the standards in the worksite.

At the same time, research can't stop; on the contrary, it must be finalized and designed as a pre-normative activity also, in order to make the protocols more precise and reliable.

In this regard, we must emphasize that the projects financed in the various European framework programs, including the current Horizon 2020, often focusing on innovative cleaning, consolidation and protection systems evidenced little impact on the quality control methods of conservation interventions.

There is still a gap in making available the most suitable assessment tools to those who are responsible for evaluating the success of an intervention. Standardization bodies cannot draft standards unless rigorous research projects oriented in this direction are launched.

In particular, standardization in the conservation of cultural heritage will:

a) improve diagnostic techniques by reducing the related costs and consequently using the saved resources to implement other conservation projects thus creating new job opportunities;
b) help to develop products, materials, tools and technologies which can be used specifically for cultural heritage conservation;
c) increase the durability of the restoration works with a consequent decrease in the frequency of conservation operations, thus reducing costs over the long term;
d) introduce equipment and technologies which are respectful of the professionals' health, of the object and are environmentally friendly. The materials/products, equipment and technologies currently used in the conservation and restoration works, or in diagnostics laboratories, are often produced by multinational corporations with great experience; nevertheless, but they haven't been produced on purpose for conservation or restoration field and, for this reason, they need to be characterised and require a specific standardisation activity.

The main problem remains the dissemination and circulation of these standards in the community of people responsible for the planning of conservation/restoration works and the professionals (restorers/conservatories and restoration companies) in charge of the treatments; therefore it would be necessary that the architects, engineers, and restorers professional associations organize training courses by inviting experts in order to explain the importance to use the above mentioned standards as appropriate specifications within the restoration/conservation projects of historic buildings.

As far as the Italian area is concerned, greater collaboration among standardization bodies, research bodies, the Ministry of Cultural Heritage and its territorial offices is desirable. Among the latter, the contribution made by the restorers is particularly useful and required, but unfortunately at the moment rather absent.

Acknowledgements

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