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Stone Consolidation in Cultural Heritage

Extended Abstracts

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Preface

After some postponements imposed by the pandemic, we welcome the possibility of the Stone Consolidation Symposium taking place in Lisbon, from 23 to 25 March. It could have been done virtually, but we all know that face-to-face discussions and bilateral contacts are moments that no virtual meeting can replace. It is our sincere hope that the rich set of communications and the generous time devoted to their presentation and discussion can be taken as a valuable reward for all those who have chosen to personally attend the Symposium.

Despite the uncertainty that the postponements brought, a large group of researchers and professionals expressed their confidence in the symposium by submitting their work to this discussion forum. The Organising and Scientific Committees are deeply grateful for their contribution to the success of the event.

The topic of stone consolidation continues to arouse great interest in the scientific community, demonstrating once again its relevance to the safeguarding of cultural heritage. With a long tradition among the research community, especially since the 1970s, and after countless published works, it is amazing how deep doubts about what stone consolidation is and how it works still persist.

Stone Consolidation 2021 will not be the end of history, but it will certainly be a milestone in it. New products have been developed and continue to be necessary, new or improved treatment protocols are required, but it is also necessary to continue questioning what is a good consolidation treatment, how to select it and evaluate its performance, both in the short and long-term. The works presented at this symposium show that our Cultural Heritage made of stone can count on the scientific community to find new ways and improve existing ones to resist the inclemency of agents of decay and the neglect to which they are so often subjected.

This book contains the extended abstracts of all submitted communications, some of which have agreed to submit a full article that will be published in e-book.

Lisbon, March 2022

The editors
José Delgado Rodrigues
Dória Costa

Keywords: Stone consolidation / Consolidation products / Consolidation protocols / Treatments effectiveness / / Treatments / compatibility / Stone deterioration

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Topics

1. General aspects on stone decay as basic input to decide on consolidation options,
2. Identification, characterisation and documentation of deterioration patterns,
3. Laboratory research on consolidants,
4. Selection of consolidation treatments. Criteria and decision-making approaches,
5. Onsite input requirements to consolidation,
6. Practical experiences on consolidation,
7. Past and present drawbacks of stone consolidation,
8. Monitoring of practical case studies,
9. New approaches in stone consolidation. Future perspectives,
10. Ethics, principles, guidelines, and other immaterial landmarks in stone consolidation,
11. History of stone consolidation.

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

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On October, 2006 a huge monolith depicting the earth goddess Tlaltecuhtli was found right in front of the main steps of the ruins of Templo Mayor, in Mexico City. This massive sculptural relief, which was carved in pink andesite stone is the largest Aztec painted monument to be discovered in Mexico, and has been considered the most important archaeological find for the last three decades. The monolith, which measures 4.17 x 3.62 x 0.38 m and weighs approximately 12.5 tonnes, is a one-eyed sculpture and was found broken into four pieces and a missing part on its central area. It was also clear, since the moment of the discovery, that some of the original colours had been preserved on its surface, but were delicate and poorly adhered to the stone.

This sculpture shows the earth goddess depicted as a woman, 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.

The stone in which Tlaltecuhtli was carved was identified by Jaime Torres Trejo as a lamprobolite andesite, composed mainly of aluminium, calcium, iron and magnesium. Pigment samples were identified by Giacomo Chiari with X-Ray Diffraction analyses as iron oxides (goethite and hematite for ochre and red), palygorskyte for the blue colour, calcite for the white colour and the black colour is assumed to be charcoal. Unfortunately, the environmental conditions contributed to the loss of most of the original binding media. However, Giacomo Chiari and Joy Mazurek could identify, by Gas Chromatography Mass Spectrometry, the presence of an orchid mucilage containing glucose and mannose.

Upon discovery, the stone fragments, which were almost completely saturated with water, were protected from direct sunlight and covered with insulating materials to prevent rapid drying. This slow and controlled drying process, which took almost one year, contributed to prevent any stress cracking, spalling or loss over the sculpture´s surface.

Once the four fragments were completely dried, they were lifted from its original place to the site street level, and placed over temporary wooden working bases previously padded with foam. After this procedure, a gatehouse and barrier for security were constructed around the fragments, and this gatehouse converted since that day in the laboratory where the subsequent conservation procedures were done.

We worked in a meticulous mechanical cleaning process for along ten months in order to remove the dried soil that covered the monolith´s decoration. As a result of this procedure, a well-preserved coloured layer emerged, and we were able to see for the first time, each one of the fragments showing a vivid original polychromy. It seemed, after detailed observations, that the mineral pigments were mixed with the mucilage used as a binder and then applied directly to the stone.

It was clear that this coloured layer was extremely delicate and unstable, and therefore, it needed to be fixed to the andesite surface. At this moment, the decision concerning on what consolidant could be used fot this procedure guided us to a research project that looked to contribute in a better understanding of the different variables and possible results. Carefully weighing the options and cautiously approaching to the best outcome, some of the conservation materials that were commonly used for stone preservation were selected as well as some natural and more compatible products. Taking also into account the final destiny that this sculpture would have, six consolidating substances were selected. Therefore, this research looked to understand the consolidation results for each one of the variables as well as their stability and their long-term behaviour.

The consolidants to be analysed were: Paraloid B72® (a synthetic polymer commonly used in conservation), Funori (a seaweed-derived adhesive chemically compatible with the original binding media), Nopal exudate slobber (a polysaccharide exudated from nopal plant, chemically compatible with the binding media), KSE 300® (stone strengthener on a silicic acid ester base, compatible with the stone), Methocel® and Klucel® (cellulosic compounds used for different conservation treatments). Small samples of the original andesite stone were painted in ochre, and fixed with each one the different substances.

The samples were treated in an accelerated ageing chamber to simulate the deterioration after time under specific conditions of humidity and solar irradiation. The purpose of this treatment was to determine how much the fixation agents could modify the pigments and/or resist the action of time. All of the samples were submitted to leaching tests, rubbing humidified cotton against the surface to measure the effectiveness of the fixation process.

Analysis by powder X-ray Diffraction (XRD) were done to identify the different compounds, Scanning Electron Microscopy (SEM) contributed to see the morphology of the different surfaces, and Nitrogen Adsorption (BET) helped to calculate the surface area and pore diameter values for each one of the samples. The results of this research guided the multidisciplinary discussions and the decisions for what we thought could be the more suitable treatment. As a result, the consolidant KSE 300®, was used in the fixation process, helping to bring stability to the original colours.

This experience shows us the importance of working among different professionals and specialists who can contribute in the discussions leading to what we considered the best decision. The analyses and studies can promote to stablish and define some new research themes concerning to similar problems using the analysed substances.

After ten years with the sculpture exhibited to the public inside the Templo Mayor Museum, we can be aware that Tlaltecuhtli´s decoration has been well preserved; and at the same time, we consider that it would be necessary to focus in a plan which addresses to some analyses and studies to the sculpture. With this future project, we would be able to define a necessary and adecuate procedure for a needed chemical cleaning process on Tlaltecuhtli´s decoration.

Bridging the gap between science and practice. Communicating research information

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Extended abstract

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 have to be immediately and unequivocally of direct 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 with alleged solutions but with insufficient justification and validation of data.

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 explicitly or implicitly present any suggestions for practical application with insufficient data validation and lack of practical demonstration.

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).

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.

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

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Nanomaterials against stonework deterioration: where are we now?

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

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 this regard, nanomaterials and nanostructures (Figure 1) provide valid tools to support the historical monument preservation (Baglioni, Carretti, and Chelazzi 2015). For example, we have successfully developed treatments based on zinc oxide and copper nanoparticles (NPs) added to conventional consolidants exploiting antimicrobial and protective properties (Ditaranto et al. 2015; van der Werf et al. 2015; Sportelli et al. 2020). On the other hand, consolidation of calcareous stones is typically achieved with dispersions of alkaline-earth metal hydroxide nanoparticles, such as $Ca(OH)_2$ NPs, because of their high compatibility with carbonatic stones and efficacy penetration through porous matrices. These nanophases could be then combined with bioactive nanomaterials. 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. Pros and cons of the proposed approaches will be also summarized, with a view on the future challenges and the development requests.

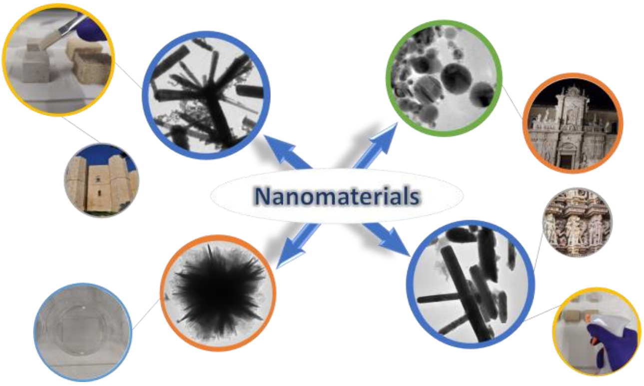

Figure 1: nanostructures for coating preparation, which are useful to fight (bio)deterioration of stone artifacts.

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Synergistic nanomaterials against stone deterioration: new routes for old problems

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KEY-WORDS: zinc oxide; calcium hydroxide; nanostructures; biodeterioration; consolidation

Biodeterioration and consolidation are two crucial aspects in the preservation of historical monuments. The growth of a wide variety of microorganisms on limestone surfaces is responsible for the formation of a biofilm, which causes long term damage of the sample (Warscheid e Braams 2000). Moreover the cohesion failure of the stone matrices results in manufact erosion (Baglioni et al. 2013). The present study aims at fighting these problems, and improving the conservation of stone artworks. Synergistic (nano)materials combining the consolidating properties of calcium hydroxide and the antimicrobial activity of zinc oxide are the target of this research. On one side, we have already demonstrated the feasibility of ZnO nanoparticles (NPs) as bioactive protecting coatings for this application (Ditaranto et al. 2015); on the other side, colloidal dispersions of $Ca(OH)_2$ NPs (nanolime) are highly compatible with carbonate stones (Baglioni et al. 2013). In this contribution, we propose a one-step synthesis of hybrid ZnO-$Ca(OH)_2$ nanostructures. This approach involves the electrochemical synthesis of ZnO NPs, based on the sacrificial anode electrolysis method (Sportelli et al. 2020; Izzi et al. 2020), integrated with the synthesis of $Ca(OH)_2$ NPs (Ambrosi et al. 2001). In particular, the $Ca(OH)_2$ NPs growth occurs simultaneously with ZnO NPs formation. In fact, the NaOH solution required for the $Ca(OH)_2$ synthesis acts also as electrolytic medium for the zinc electrode corrosion. Hence, the zinc electrode is immersed in the alkaline solution and $CaCl_2$ is added slowly during the electrosynthesis. The process is performed under continuous stirring for 1 h, at 80°C in deaerated conditions. The as-prepared powder is dried overnight at 120°C. Spectroscopic (FTIR) and morphological (TEM) characterizations are reported in figure 1. The IR spectrum shows both the typical feature of $Ca(OH)_2$ at 3642 cm^{-1} (green band) and the ones of ZnO around 500

cm^{-1} (yellow band). The morphology of hybrid nanomaterials reports $Ca(OH)_2$ polyhedral structures with sizes ranging from 500 nm to 200 nm, as well as agglomerated spheroidal ZnO NPs. As preliminary experiment, the hybrid nanomaterials were brushed on sanded glasses, in order to investigate the features of the innovative coatings in terms of contact angle and carbonatation process.

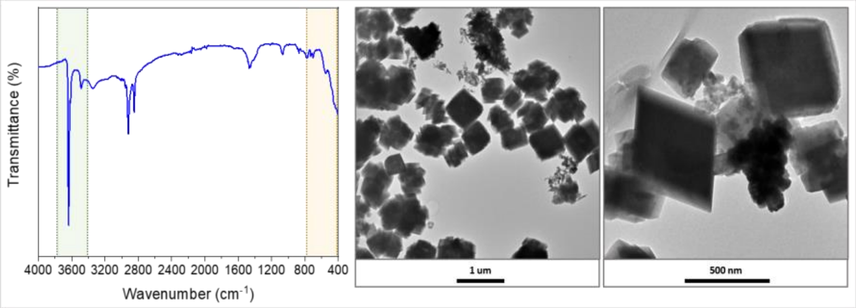

Figure 1: IR spectrum and TEM images of ZnO-$Ca(OH)_2$ nanostructures.

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

The Ducal Palace of Vila Viçosa, headquarters of the Most Serene House of Braganza, is one of the most notable 16th century manor houses still existing in the Iberian Peninsula. This article will focus on its magnificent façade – which is completely covered with white and Ruivina marbles from the Estremoz Anticline – contributing to the debate on topics of stone cleaning and consolidation (methods, materials, criteria).

Vila Viçosa was chosen as the setting for the Commemorations, in 1940, of the Centenaries of the Foundation of Portugal (1140) and of the Restoration of Independence (1640). The impressive façade should serve 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 Directorate-General for National Buildings and Monuments (DGEMN) technicians argued for the cleaning and "repair" of the stonework of the main façade, including the replacement of some broken pieces. At the time, the interventions on monuments were, in accordance with DGEMN guidelines, mostly aligned with the principle of "style unity" defended by the 19th century architect Viollet-le-Duc, which led to somewhat radical restorations that sought to retrieve the "original beauty" of the buildings. The approach adopted in Vila Viçosa is 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.

The technical description written on the occasion (1939) and the report of the Superior Council for Public Works (CSOP) (1940), both unusually detailed documents for the time, establish the action criteria: cleaning with safeguarding of the golden patina of time; removing any accumulated plants and dirt with the use of "pointer trowels", and resealing the joints with a grout made of hydraulic lime and sand; and the replacement of stones - the new marbles should, as far as possible, resemble the colour and appearance of the original after having been briefly cleaned. Such restrained cleaning "should not", according to CSOP, "involve the use of grinding wheels nor wire brushes, but only common water and piassava". If it was carried out, the stone consolidation (for restoring its cohesion and adherence) was probably achieved through injections of fluid grouts, then common practice in most of DGEMN interventions; and the stones attached, like in other monuments, with a strong plaster made of cement and sand, along with, perhaps, rustless brass "staples".

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 – House of Braganza's property – was handled, the actual intervention only began after the 1940 celebrations, after the Administrative Board of the House of Braganza Foundation took office in January 1945, with the works resumed as they had been planned in 1939. Raul Lino, then chief architect of the Department for Studies and Works on Monuments of DGEMN, authored the intervention plan which aimed to adapt the building into a Museum-Library. The intervention on the façade took place in 1945 and was among the first works made. Lino's criteria for this intervention were made clear when he stated "…we take no interest in plumb lines nor in rigorous alignments, but in ensuring the permanence of what already exists". Critical of "style unity", Raul Lino, aligned with the most recent international ideas, plays an essential part in transforming the practice of conservation and restoration of monuments. He opts to respect the pre-existing structures and materials, excluding "radical technical restorations" or imitations that may "be deceiving regarding the time of their execution". In line with CSOP experts, Lino declares that "a special importance was given to the conservation of the appearance of the monument", "we are concerned with preserving its evocative value".

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, revealing changes in the most radical action paradigms of DGEMN.

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Effectiveness and durability of the silico-organic treatments applied to silicified sandstones and conglomerates

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Introduction

In this work, a multivariate statistical design was performed using a Canonical Biplot to determine variations in the ultrasound propagation speed in three spatial directions (Vx, Vy, Vz) and the chromatic coordinates (L*,a*,b*). This information was used to determine: a) the durability of the treated and untreated quarry samples after the application of freezing/thawing and colding/heating processes (-20 / 110ºC) (Iñigo et al., 2013) and b) the effectiveness of different silico-organic treatments [(H224, RC70 and RC80) applied to the fresh quarried stone samples (Iñigo et al., 2020).

Materials and methods

This work was carried out on fresh samples of silicified sandstone (TG, TB, TO, TR) and white conglomerate (Z1) quarry from Zamora, Spain (Añorve, 1997). The stones were treated with conservation treatments [H224 (alkylpolysiloxane oligomer), RC70 (ethyl silicate) and RC80 (ethyl silicate, methyl resin and resinous polysiloxane that is hydrophobic)] (García-Talegón et al., 2015; 2016) and/or processes of freezing/thawing and colding/heating (− 20/110 °C) aging (Iñigo et al., 2013). Color was measured using a Minolta model CR-310 colorimeter specific to solid materials and the ultrasound propagation speed using a STEINKAMP model Ultrasonic Tester BP-5.

The Canonical Biplot analysis has been carried out on a matrix of 400 rows and 6 columns (L *, a *, b *, Vx, Vy, and Vz), where the rows are grouped into 40 groups with the following names: **STX**, where **S** is the type of quarry sample (Z1, TG, TB, TO and TR), and **TX** (T0, T1, T2, T3, T4, T5, T6, and T7), where: a) T0 = Quarry samples, b) T1 = Quarry samples subjected to freezing/thawing and colding/heating aging, c) T2 = Quarry samples treated with H224, d) T3 = Quarry samples treated with RC70, e) T4 = Quarry samples treated with RC80, f) T5 = Quarry samples treated with H224 and subsequently subjected to freezing/thawing and colding/heating aging, g) T6 = Quarry samples treated with RC70 and subsequently subjected to freezing/thawing and colding/heating aging and h) T7 = Quarry samples treated with RC80 and subsequently subjected to freezing/thawing and colding/heating aging.

Results and discussion

In most of the cases studied, the ultrasonic propagation speed decreased in both the untreated samples and those treated with the conservation products after carrying out the aging process. Moreover, it was found that the ultrasonic propagation speeds were lower in untreated samples than in treated ones. Ultrasonic propagation tests indicate that the treated samples are more durable than the untreated fresh samples. Also, the chromatic coordinates of the treated samples, in general, were darker (↓L*), redder (↑a*) and more yellow (↑b*) with respect to the untreated samples. As an example, the figure corresponding to the TG sample of silicified sandstone is given (Fig. 1).

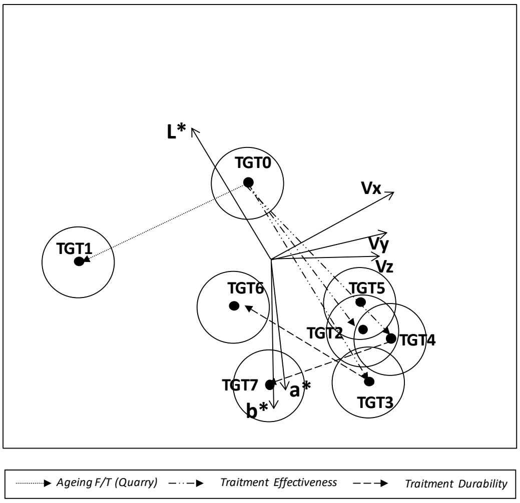

Fig. 1: Canonical Biplot for the stone variety TG (axes 1 and 2).

The order in durability of the quarry materials after being subjected to freezing/thawing and colding/heating aging decrease was:

TG > Z1 > TB ≈ TR ≈ TO

indicating that the greater the grain size of the minerals (TG and Z1), the greater the decrease in the ultrasound propagation speed, Fig.1. Additionally, no variations were observed in samples TB, TO, and TR, Fig. 2, as these are the most porous stones (Iñigo et al., 2020) with a large number of pores greater than 5 µm. The process of freezing/thawing did not cause a disruptive effect, because drainage occurred, as well as the expulsion of fluids within the advance line of the freezing front (Winkler, 1973).

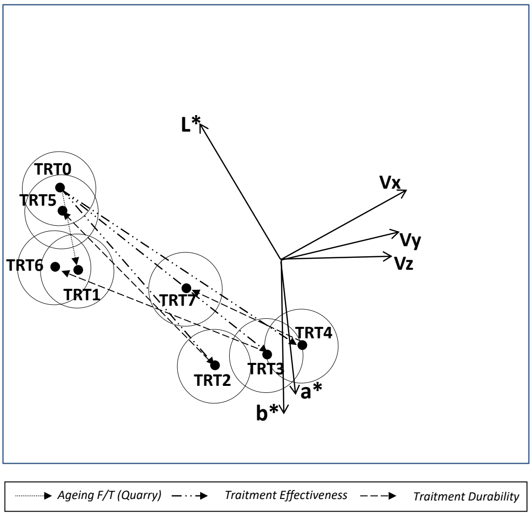

Fig. 2: Canonical Biplot for the stone variety TR (axes 1 and 2)

In the durability of the treated samples after being subjected to freezing/thawing and cooling/heating aging, there is a curious fact in the TR sample, Fig. 2. If we analyze the ultrasonic propagation speed, the conservation treatments used do not improve the durability of the treated stones compared to those of the fresh quarry samples, except in the samples treated with RC80. This is due to the fact that the TR sample has the highest porosity of all those studied (Inigo et al., 2020). This means that the consolidation products (RC70 and RC80) can be introduced in greater quantities and more easily into the interior of the rock. When performing the 25 aging cycles, the products can be eliminated by being easily dragged to the surface since most of their porosity is directly interconnected with the surface of the specimens (AC > 90%, Inigo et al., 2020), but it seems that the RC80, having in its composition a waterproof part, makes this process slow down, presenting a slightly higher durability compared to the corresponding quarry rocks, which is significant ($p < 0.05$).

Regarding the effectiveness of the treatments applied, Fig. 1 and 2, in general, we can conclude that:

1) Treatment with H224 (T2) produced the least effect on all samples due to the way in which it was applied, using a brush did not allow it to properly penetrate into the stone and to form a thin film that prevented water from entering.
2) In the case of the consolidation treatments RC70 (T3) and RC80 (T4), where maximum penetration was required, the effects were very similar, being more so with RC80.

Conclusions

The analysis of the results obtained by means of the Canonical Biplot analysis, has allowed us to draw the following conclusions:

a) Most of the variations found are obtained after the applying the treatments. The order of effectiveness of the conservation products applied is:

RC80 > RC70 > H224.

b) The accelerated aging applied to the fresh quarry samples studied decreases the speed of ultrasound propagation in all cases. Additionally, the ultrasound propagation speed increases in the treated samples compared to fresh quarry samples. Finally, the ultrasound propagation speed is reduced, in general, in the samples treated and subsequently aged using a freezing/thawing and cooling/heating treatments, but many exceptions occur.

c) The changes in the chromatic coordinates (L *, a *, b*) are not greatly appreciable in all of the variables and treatments applied for each of the samples, except for the sample TR.

d) The changes observed in the ultrasound propagation speed variable, between the fresh quarry samples and those treated after using the freezing/thawing and cooling/heating treatment indicate that the durability of the treated samples is greater than that of the fresh-quarried stone. This indicates that, in most cases, the treatments are effective when using these types of stones.

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Glycol Alkoxysilanes-Chitosan Hybrids in Stone Conservation

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KEY-WORDS: glycol alkoxysilanes, chitosan, hybrids, stone conservation

EXTENDED ABSTRACT

Stone consolidants have been widely used in order to protect historical monuments. Consolidants and hydrophobic formulations based on alkoxysilanes have been an alternative mostly using tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) and alkylalkoxysilanes as precursors, [1] silanes that are not soluble enough in water and it is necessary to add an organic solvent. In the search of other silicon derivatives with potential use in this field, it is suggested to use tetrakis(2-hydroxyethyl)silane or orthosilicate (THEOS) and tris(2-hydroxyethyl)methyl silane (MeTHEOS) as precursors because they are water soluble[2]. Additionally, it has been reported THEOS is compatible with different natural polysaccharides and the same behavior is expected for MeTHEOS [3]. The approach is to use both glycol modified alkoxysilanes to obtain hybrid consolidants and hydrophobic formulations-chitosan (as polysaccharide) with the following main goals: the use of water soluble silanes in stone conservation based on both silicate and calcareous composition [4]. In the case of calcareous building stones is well known the non-compatibility with alkoxysilanes based formulations [1] and it is expected to solve it by using chitosan. The glycol modified alkoxysilanes were obtained by the most reported esterification of TEOS or MTEOS with ethylene glycol [2]. Several reports in literature refer studies regarding the system THEOS-chitosan but the characterization as well as the way they interact as far as we know has not been studied in detail and quite recently, we have been able to elucidate such interaction [4]. Some examples of hybrid consolidant and hydrophobic formulations applications will be presented. The surface modification of different substrates, mainly building stones from historical and archaeological sites from the Guanajuato city and state was studied. Having in mind the required evaluation, several chemical and physical analysis have been performed in order to assessing the effectiveness and compatibility of the suggested hybrids on carbonate and silicate substrates [5]. Regarding the application to different stones both siliceous and/or calcareous composition, intrinsic fluorescence emission of chitosan seems to be important to find out the efficiency of consolidant or hydrophobic formulation distribution inside or in the stone surface [5]. The formulation based on glycol alkoxysilanes-chitosan preserve the chitosan fluorescence property. The authors wish to acknowledge CONACYT-México (Project 284510), supported by the Fondo Sectorial de Investigación para la Educación, by the program Becas de Posdoctorado por México and the University of Guanajuato (Guanajuato-México).

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

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KEY-WORDS: Chafariz da Glória, Itacolomy quartzite, stone degradation, characterization, damage mapping.

The Chafariz da Glória is one of the many existing fountains in Ouro Preto, MG, Brazil, built in the 18th century, 1872 (Carvalho, 1936) with the function of meeting the needs and difficulties of water supply. Its main construction material is the Itacolomy quartzite, present in both its fitting and decorative elements. Currently deactivated, it fulfills the role of documentary, historical and cultural record in the city's urban landscape. Due to its relevance, all possible efforts need to be adopted in the preservation and conservation of the Monument.

The fountain is of the parietal type, in support, built into a section of the slope with accentuated global declivity that descends from Rua Getúlio Vargas (Centro) towards Rua Antônio Albuquerque (Bairro Pilar). Over the years, it has been through several maintenance, conservation, restoration and even some alteration procedures. Characterizing the building materials that make up the monument, and relating them to the works carried out to date, especially the one that occurred in 2015, as well as the current damages and those that have recurred over the years is essential for proposing more lasting solutions and permanence of the monument as a cultural record for even longer.

This work put into evidence the first investigations about the causes and agents that have motivated the degradations suffered by the stone material used in the Monument, the Itacolomy quartzite. Initially, a detailed survey of the history of the Chafariz was carried out, based on bibliographic and iconographic research, including the various conservation and restoration interventions carried out over the years (in the 20th and 21st centuries). The research also made it possible to obtain information about the area of extraction of the stone material used.

In the next phase, a mapping of the damages was carried out based on the identification and description of the current degradations, visual identification and through observations in cultivation slides of possible biological agents combined as well. Such mapping allowed to make a preliminary relationship between the degradations with their motivating agents and causes, and these with the characteristics and properties of the stone and the interventions that the fountain has undergone until today.

In its current state, the Chafariz da Glória has no damage that could compromise its structural stability. However, it presents degradations in the stone material mainly in the parts that make up the fountain body, such as the base, columns and figureheads that can be considered worrisome, There is the presence of erosion, detachment of isolated grains, rounding of edges and vertices of quartzite blocks, appearance of blistering, exfoliation, scaling and disaggregation, concentrated mainly in the corner vertices on the left side, more precisely on the shaft, and the presence of microalgae between the desquamation plate and the integral stone (Figure 1).

Figure 1: (a) Front view of Chafariz da Glória, Ouro Preto-MG; (b) detail of the stuffing; (c) blisters and colonization by microalgae and mosses. Source: authors' file, 2020.

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. It was possible to observe colonization by microalgae, fungi, lichens, mosses, ferns and other plants, including the invasive herbaceous plant popularly known as the English carpet, Polygonum capitatum Buch.-Ham. These colonizations 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 the biodeteriogenic actions caused by these agents one can identify the release of acidic substances, moisture retention and mechanical damage to the stone, the last element being mainly associated with larger plants. Some biofilms that are strongly adhered to the stone surface, which has allowed the deposition of particles, are favoring the emergence and development of new crusts.

The characteristics of the Itacolomy quartzite stone used in the Monument and verified in the material obtained in the extraction area, such as the absorption capacity and higher porosity, have also contributed to make the stone more susceptible to degradations when exposed to an environment with constant humidity (Costa, 2009) due to the low recrystallization and compaction rate. The presence of clayey material in the stone also contributed to the degradations. In the presence of moisture, these clays expanded, generating swelling and causing, for example, sanding. Thus, the disaggregation present in the Chafariz can be understood as response to the persistent action of moisture.

In view of the investigations carried out so far, it has not been possible yet to clearly establish any contributions or the relationships of the conservation procedures and their substances applied in the last restoration intervention, in 2015 that can explain the aggravation of the conservation status of the Monument.

For future proposals of consolidation solutions for the Chafariz da Glória, which mean a longer-lasting conservation, the next phase of the research intends to advance with studies on the extent and scope of the damage already caused to the building element, to know the source of moisture and detail the areas in which its performance is more or less significant and finally to seek the salts identifications in case their presence is confirmed.

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Efficacy and compatibility of silane-based consolidants on limestone

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KEY-WORDS: limestone; silanes; incompatibility risks; aesthetic; water transport.

INTRODUCTION

Restore the cohesion of loose stone particles, biding them and securing into the underlying sound stone is the primary and ultimate scope of stone consolidation. However, it is crucial to guarantee the best compatibility to avoid harmful side effects that can irreparably jeopardize the value of the object. It is important to have in mind that a completely compatible or completely incompatible solution does not exist (Delgado Rodrigues and Grossi, 2007).

Carbonate stones are the most abundant varieties in built heritage but also the most problematic ones to consolidate (Sena da Fonseca *et al.* 2018). This investigation compares the overall performance of a set of silane-based consolidants on a well-known and historic limestone.

MATERIALS AND METHODS

Ançã stone (soft limestone) was treated with five silane-based consolidants having different specificities (dry residues, secondary active constituents, etc.) with the same procedure to obtain comparable amounts of product absorbed.

Drilling resistance was used to access the potential of the consolidants to be effective and access the compatibility between the mechanical properties of the consolidated and unconsolidated zones. The treating ability of the consolidants, visual properties and hydrophilic behaviour of the treated stones were the other compatibility criteria assessed.

RESULTS AND DISCUSSION

Treatments exhibited very different tendencies to increase the superficial and in-depth cohesion of the stone. A wide range of situations were observed, from soft cohesion increments in-depth to superficial hardened layers.

All consolidants revealed good treating ability, but the formation of these hardened layers can sometimes create incompatibility problems.

The potential of the treatments to change the original properties of the stone in terms of aesthetics and hydrophilic behaviour was also very variable. Treatments whose consolidants have lower dry residues tend to affect less the colour of stone surface and their water transport properties; however, the differences obtained seem to be explained not only by the amount of dry residues left in pores but also by the chemical specificities of the consolidants.

Although the application procedure had an important role on the overall compatibility of the treatments, the treatments performed with a group of silane-based consolidants were placed in an intermediate position of an incompatibility degree scale, i.e., are between the hypothetical completely compatible and completely incompatible action. The other group of treatments are closer to the completely incompatible side due to their influence on the initial water transport properties.

CONCLUSIONS

Silane-based consolidants revealed to be very versatile in terms of cohesion increments, solutions capable to fill a significant range of situations were obtained, i.e., from cases where soft cohesion increments in-depth are advisable to situations where only superficial consolidation is needed.

Although silane-based consolidants products have the same main constituents, chemical particularities can cause dramatic changes on their overall performance.

This investigation characterized the impact of several treatments and identified the pros and cons of each one to contribute for a more supported decision on the selection of consolidants to treat historical built objects of soft limestone.

AKNOWLEDGMENTS

Fundação para a Ciência e Tecnologia (FCT) for funding the Project NanoCStoneH - Innovative nanocomposite for the conservation and consolidation of carbonate stone heritage - (PTDC/ECI-EGC/29006/2017), and the research units CERIS and CQE (UIDB/00100/2020).

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Behaviour of silane-based consolidants on mineralogically different porous stones

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KEY-WORDS: carbonate stone; silicate stone; silanes; mineralogy; porometry.

INTRODUCTION

Sedimentary porous stones are generally easy to cut and carve and therefore were extensively used in buildings, statues and monuments for many millennia, being still used in numerous modern constructions. Today, some of those stones are severely degraded and part of them are susceptible to be tackled through consolidation actions. Silane-based consolidants can be an option to proceed with such interventions, however, their performance can be affected by multiple factors. The contrasting performances on silicate and carbonate substrates are overused in literature as an example of such dependence even if just few recent studies have directly compared silane-based products on stones of both natures (Ban *et al.* 2019).

The present study analyses and compares the behaviour of three recent silane-based products into mineralogically different porous stones with noteworthy presence in Portuguese built heritage (limestone and sandstone).

MATERIALS AND METHODS

One commercial consolidant and two consolidants developed within the frame of NANOCSTONEH project were applied into power (obtained by stone griding) and specimens of Silves sandstone and Ançã stone. The three consolidants are pre-condensed and catalyzed silane-based consolidants.

The analysis of dry powder blends and treated specimens was performed by analytical techniques (e.g. ATR-FTIR, mercury intrusion porometry), FEG-SEM and mechanical testing (hardness and drilling resistance).

RESULTS AND DISCUSSION

Unambiguous signs of chemical interactions between consolidants and stone minerals were not unveiled, but the mineralogical nature caused minor variations on the aggregation mechanisms of the powders. If the consolidant has potential to form well-adhered thin silica structures bonding adjacent grains, it occurs for both, silicate and carbonate powders. Cohesive powder blends were obtained for both cases.

Consolidation materials were well adhered to minerals of sandstone specimens and conformed the minerals of limestone specimens. The good adhesion caused strength increments on both types of stones but an overall better potential for success was found for sandstones. The wider pore size distribution was fundamental to explain slightly different efficacies since the deposition of consolidation material also occurs into smaller pores, where the bridging and filling capacity of the consolidant is less important and the strength increase can be enhanced. Nonetheless, the potential of the consolidants is primarily affected by its catalytic route and amount of dry residue while differences on stone intrinsic properties are minimal when compared with the impact of these factors.

CONCLUSIONS

The comparative consolidation efficacy points out an overall better potential for success in sandstone than in limestone, however, this does not necessarily mean that alkoxysilane-based consolidants are more effective in silicate stones than in carbonate stones. In fact, alkoxysilane-based consolidants can produce highly cohesive silicate or carbonate monoliths and the efficacy is primarily affected consolidants specificities and stone porometry.

From a practical viewpoint, silane-based consolidants are good candidates to consolidate either degraded historic sandstone or limestone objects since revealed potential efficacy and minimal alterations on the original porosity or pore size distribution.

AKNOWLEDGMENTS

Fundação para a Ciência e Tecnologia (FCT) for funding the Project GreenMAP (PTDC/ECI-EGC/2519/2020), and the research units CERIS and CQE (UIDB/00100/2020).

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Assessment of the effectiveness of ethyl silicate-based consolidants on weathered archaeological limestone from Jordan

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KEY-WORDS: Consolidation, ethyl silicate, limestone, Ultrasonic technique, Jordan.

In this study, the effectiveness of ethyl silicate-based products for the consolidation of weathered archaeological limestone is investigated and assessed. Four varieties of naturally weathered limestone samples were selected from architectural structures in three archaeological sites in north and northeast Jordan. The selected stone samples were characterized for their petrographic, physical and mechanical properties using several traditional and non-destructive testing methods including mercury intrusion porosimetry, capillary water uptake, water vapor diffusion resistance, thermal expansion coefficient, biaxial flexural strength, drilling resistance, and ultrasonic technique. Two silicic acid ester commercial consolidation products namely, Remmers KSE 300 and Remmers KSE 300HV, were selected and applied on the studied stone samples. The two selected products have almost the same characteristics, except that the latter contains an extra coupling agent for particular applications to limestone. The effectiveness of the applied consolidants was assessed by studying the changes in the properties of treated stone, on bulk samples and in depth profile, as compared to the untreated unweathered stone. The tested consolidation products seemed to be effective in terms of improving the physical and mechanical properties of the stones. However, the product containing coupling agent provided better results, particularly with regard to the properties of stone in depth-profile as shown in the figure and tables below. The results from ultrasonic velocity measurements agreed satisfactorily with those from traditional physical and mechanical tests and this technique proved to be effective for assessing the effectiveness of consolidation treatments.

Examples of selected figures and tables from the study are shown below:

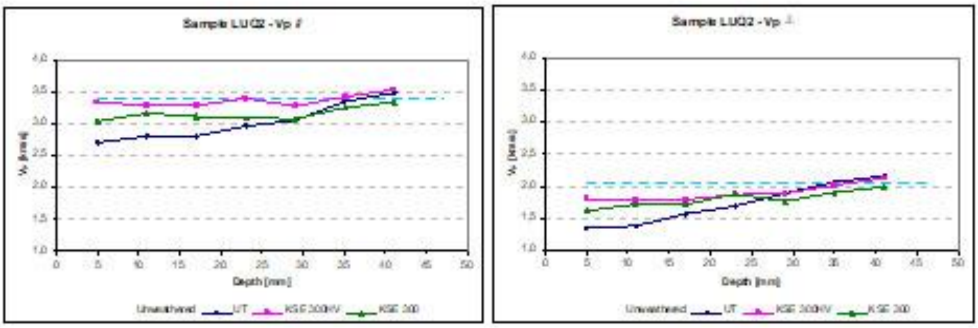

Figure 1: Ultrasonic pulse velocity in depth profile of a weathered and treated sample measured in two directions (parallel and perpendicular to beddings) with ultrasonic frequency of 350 kHz.

Table 1: The weathering and penetration depths of consolidants as measured by ultrasonic velocity measurements.

Sample	Weathering depth [cm]	Penetration depth [cm]	
		KSE 300	KSE 300HV
LH	1 - 1.5	1.5	1.5 - 2
LJ2	3	1.5	3
LJ3	2.5	2	2.5
LUQ2	3 -3.5	2.5 - 3	3 - 3.5

Table 2: The overall assessment of the effectiveness of consolidation treatments

Property	Requirement (Snethlage and Wendler, 1995; and others)	KSE 300	KSE 300HV
W-value	$W_t \leq W_u$	+	+
μ-value	Increase ≤ 20%	+	±
Drying	No increase in drying duration	+	+
Color	$\Delta E^* \leq 5$	+	±
α_T	Increase ≤ 20%	+	±
Penetration depth	Deeper than the weathered zone	±	+
DR	Homogenous strength profile	±	+
β_{BFS}	Homogenous strength profile	±	+
$E_{stat/dyn}$	$E_t \leq 1.5\ E_u$	±	+
US V_P	Homogenous strength profile	±	+

+ good; ± fairly good; - not acceptable

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Going Beyond the Recommendations: Practical Applications of Large-Scale Chemical Consolidation Treatments

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Extended Abstract

With the integration of chemical consolidation into the standard toolbox for stone, difficulties with large-scale application are emerging for conservators. While its mechanical properties have been widely researched, practical implementation is often not evaluated outside laboratory or small-scale applications.

The purpose of this presentation is to share the experiences and lessons learned when confronting the implementation of consolidation on a large scale. The authors' goals are to provide the groundwork for what to expect and how to approach anticipated challenges, even setbacks, to better prepare contemporaries that may take on this task.

The presenters are speaking from personal experience with consolidation of white, carved marble using a hydroxylating conversion treatment followed by ethyl silicate consolidation. Techniques have evolved while working at the Russell Senate Office Building, Washington, DC, Vermont Marble at the Carnegie Library, Washington, DC, and Lee, Cockeysville, Georgia, and Vermont marbles at the US Capitol, North and South Extensions, Washington, DC. While this is the basis of their experience, the overall themes can be applied to other consolidants applied to a range of stone substrates at a large scale.

Chemical consolidation poses logistical challenges when applied at a building scale. Those challenges break down into four categories during large-scale implementation: site protection, training, application, and environmental controls. These considerations are critical to a successful consolidation treatment. When approaching a major consolidation project, it is important to have realistic expectations on the goals and the implementation. By setting expectations for the whole team, everyone will be able to anticipate the obstacles and be ready to problem solve as challenges arise.

The site protection for collection of runoff and protection of surrounding materials and the public is the most time-consuming aspect consolidation that has been refined over many projects. This presentation will discuss the evolution of EverGreene's large-scale site protection, including storage of chemicals, containment of chemical runoff, and protection of surrounding areas during chemical preparations.

In order to achieve the most desirable results, consolidation treatments must follow technical guidelines given by the manufacturer as closely as possible. The specifications

are typically replicating testing methods achieved in a lab setting. The crew on site must adhere to the specifications to achieve “laboratory” results. This requires the crew to understand the timing, application technique, and restrictions related to the treatments (i.e. exposure to sunlight, water, temperatures). The crew does not necessarily need to be educated on the chemical reactions that are occurring, but they need to have enough understanding in order to recognize the importance of the restrictions specified. We will review our approach to staff training and awareness.

Controlling the environment on a multi-level scaffolding presents challenges that both conservators and contractors are unaccustomed to handling. EverGreene has explored communication techniques such as “call and responses”, hand signals, and flags to coordinate staff across scaffolding. Consolidating year-round has forced staff to think of creative ways to maintain temperature and relative humidity.

Standardization has become a double-edged sword. The nature of specifications has made it difficult to meet the rigid contract requirements that are common on large-scale construction projects. Second to this, increased environmental awareness and a comprehension of the dangers of the consolidation chemicals is needed to enhance current site protection and material handling practices. Often, these structures remain occupied and the health and safety of both workers and occupants must be evaluated.

Another factor to evaluate is the scientific and technical nature of chemical consolidation. These elements, so familiar to conservators, must be addressed and understood by professionals outside the field of conservation. This poses its own challenges to ensure a collaborative outcome. Different levels of communication with both stakeholders and staff is required during the pre-project planning and implementation phases during the project. The balance communicating both the technical aspects of consolidation and the logistical concerns will be discussed.

This presentation will discuss our team’s collective experience in North America with the application of chemical consolidants on large-scale masonry façades. We will review successes and failures in methodology with a focus on the four main logistical challenges (training, site protection, application, and environmental). Lastly, we will discuss our recommendations for future applications.

KEY-WORDS: large-scale, lessons learned, managing expectations.

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

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Since recent years, inorganic nanoparticles have been explored for a use in alternative to traditional consolidants. Several advantages rely on nanoconsolidants. In particular, nanosilica dispersions require a shorter curing time compared to ethyl silicate based consolidants [Scherer & Wheeler, 2009) and consolidating effectiveness is not highly influenced by moist substrates and humid environment [Zornoza-Indart & Lopez-Arce, 2016]. One main issue is the limited ability to penetrate deeply into the substrate, [Licchelli et al., 2014]; the solvent used as dispersion medium may play a significant role in this regard [Sassoni et al., 2018].

Here we report on an experimental activity dealing with nanoSiO_2 in an alcohol dispersion applied to a highly porous stone. The study aims to assess the treatment issues compared with those previously obtained from the same nanoparticles in water, in order to investigate the role of the solvents in the transport mechanism of silica NPs in porous materials.

Nanosized SiO_2 dispersed in a water/alcoholic solution (17% w/w, density of around 1.0 g/ml, viscosity of 10 mPa/sec at 20°C and pH of 8.0) was used. The precipitation of the silica was obtained by 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. Silica powder was then cleaned with distilled water, dried and re-dispersed in water. A stable nanodispersion of rounded NPs having a mean size of approximately 35 nm (PdI 0.20), was obtained and finally mixed with ethanol. The treatment was applied on a soft limestone made of fine bioclastic remains and lythoclasts within a micritic groundmass and poor amounts of a fine calcitic cement. 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 previously selected, namely consecutive steps by brush.

Penetration depth was studied through SEM-EDS analysis, using Si as a marker of the product within the stone, and consolidation effectiveness was assessed by a low destructive penetration test using an RSM (Response Surface Methodology) penetrometer, and UPV propagation. Surface colour changes were measured by colorimetry and variations of the stone microstructure by Mercury Intrusion

Porosimetry. Stone behaviour with water was evaluated through wettability measurements, water capillary absorption and vapour permeability tests.

EDS maps and distribution profiles of Si, showed an accumulation layer of nano-SiO2 just under the surface, with a penetration depth mostly up to 50 µm from the surface.

A weak hardening effect due to the presence of the nanosilica accounts for the results of the penetrometer test, which recorded the penetration depth of the tip lower in the treated stone (3.02 mm) compared to the untreated one (4,33 mm). No changes in UPVs were recorded, meaning that the treated stone layer had a negligible incidence on the wave propagation, due to the poor penetration of the product into the stone.

Colorimetric measurements detected small variations for L*, a* and b* coordinates on the stone sample after the treatment and overall colour change values (ΔE*) under 1.

Porosimetric analyses, aiming at evaluating the effect of the nanosilica filler on the stone microstructure, showed a slight reduction of the presence of pores with radii between 0.5 and 0.1 µm (13%) in the treated specimens and meaningless variations of the integral open porosity (9%). Indeed, the stone was investigated over a sample thickness of 5 mm from the treated surface, notably higher than the thickness involved in the treatment, so that the detected modifications are likely underestimated.

The application of the nanosilica strongly changed the stone surface wettability. Contact angle values were null on the untreated stone, as water absorption was very high and rapid, and no drop formed on its surface. After the treatment the mean value was 31.42°±3.60°. The presence of the consolidant was found to decrease the kinetics of the water uptake by capillarity by a mean of 41%, while the overall amount of water absorbed remained almost unchanged or slightly reduced after treatment up to a maximum of 6%. Water vapour permeability increased by 7% in the treated stone. This result suggests that rather than pore occlusion a probable lower condensation phenomenon on the hydrophobic pore walls took place, leading to an increase of the diffusion rate of water vapour through the pore structure.

The obtained results strongly differ from those previously obtained with the use of nanosilica in water dispersion [Vasanelli et al., 2019]. Better treatment performances in terms of penetration depth and consolidation effectiveness were obtained in that case. 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. However, the nanoparticle accumulation does not act as a barrier against the water absorption by capillarity, nor against the vapour transfer.

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The Consolidation of a Variety of Vermont Marble

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KEY-WORDS: Conservare OH100, FUNCOSIL 500 STE, ammonium oxalate, ammonium tartrate, HCT, Vermont marble, thermal stress

Since the nineteenth century Vermont marble has been one of the most commonly used stones for monumental sculpture and architecture in the United States. It is a fine-grained calcareous marble with varieties that range from pure white (similar to Carrara marble) to highly veined with accessory minerals. At the Carnegie Library in Washington, DC, USA, much of the highly-veined Vermont marble had become highly deteriorated – exhibiting poor mechanical strength and severe granular disintegration. Specimens were extracted from the building for evaluation of the performance of four consolidants: 1. ammonium oxalate (*ad hoc* formulation); 2. diammonium phosphate (*ad hoc* formulation); 3. ammonium tartrate (*HCT*) followed by *Conservare OH100*; 4. *FUNCOSIL 500STE*. A group of specimens are also left untreated. Treated and untreated specimens were subjected to cold- and hot-temperature cycling: 1. -20 °C to 20 °C and 2. 25 °C to 55 °C each for 100 cycles.

Four methods were used to evaluate the performance of the consolidants on this particular stone: 1. colorimetry; 2. microabrasion; 3. biaxial flexure strength testing; 4. water vapor transmission. Table I summarizes the results obtained using these methods. It should be emphasized that there are no standards that indicate if a change in performance with respect to a specific test method can be considered sufficient, insufficient, or excessive. The result of testing are summarized in Table I.

Changes in color are globally expressed as ΔE using the CIELab system. ΔE takes into account changes in lightness-darkness, red-green, and blue-yellow of specimens. Color changes ranged from a low of 0.387 for the uncycled ammonium phosphate treatment to a high of 5.37 for the cold-cycled *FUNCOSIL 500 STE.* On average, color changes were relatively low across all consolidants and all conditions. Most of the color change for most of the specimens involved darkening.

Reductions in losses using the microabrasion method ranged from 38.3% to 73% for consolidants other than ammonium oxalate, which averaged only 20% across all three conditions.

Strength increases were highest for treatments employing alkoxysilanes – *HCT + Conservare OH100* and *FUNCOSIL 500 STE* – ranging from 99.1% to 138% and were not significantly reduced with either cold- or hot-temperature cycling. Ammonium oxalate produced the lowest strength increases under all conditions.

Water vapor transmission rates were most affected using *FUNCOSIL 500 STE* (34.8%) and least affected using *HCT + Conservare OH100*.

Test Method	**Thermal Conditioning**		
	Uncycled	**Cold cycling**	**Hot cycling**
Colorimetry testing (ΔE from untreated specimens)			
Ammonium Oxalate	3.56	3.12	2.61
Diammonium Phosphate	0.387	2.65	2.33
Funcosil 500STE	1.69	5.37	0.887
HCT-*Conservare* OH100	1.26	3.97	0.565
Reduction in weight loss using microabrasion (%)			
Ammonium Oxalate	19.7	16.5	24.0
Diammonium Phosphate	59.2	73.0	58.0
Funcosil 500STE	58.0	62.2	67.1
HCT-*Conservare* OH100	48.2	61.0	38.2
Increase in biaxial flexural strength (%)			
Ammonium Oxalate	11.6	29.8	26.6
Diammonium Phosphate	76.0	87.5	40.4
Funcosil 500STE	108	138	137
HCT-*Conservare* OH100	104	138	99.1
Reduction in water vapor transmissivity (%)			
Ammonium Oxalate	11.2	n.d.	n.d.
Diammonium Phosphate	24.2	n.d.	n.d.
Funcosil 500STE	34.8	n.d.	n.d.
HCT-*Conservare* OH100	4.35	n.d.	n.d.

Table I. The four consolidants were evaluated using four test methods and are summarized in the above table.

In addition to the above-described methods and results, concerns have also been expressed in the stone conservation literature about the increase in elastic modulus of consolidated stone *vs.* the unconsolidated substrate. The alkoxysilane-based consolidants produced (and retained) the highest strength increases while the reactive water-based consolidants produced lower strength increases. For the alkoxysilane consolidants and diammonium phosphate, higher elastic moduli were produced along with higher strengths. The ammonium oxalate consolidant produced a much lower elastic modulus – similar to untreated marble along with lower strengths.

The Design and Implementation of a Testing Program for Marble Consolidation

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KEY-WORDS: marble, alkoxysilanes, nanolime, thermal stress

Marble has been one of the most important materials for art and architecture for nearly five millenia. In the Medieval period, one of the finest examples of the use of marble are the sculptures and architectural elements in the cloister of the *Church of San Trophime* in Arles, France. As part of a larger conservation effort, research was carried out on the consolidation of the Carrara marble employed at the cloister. A stock of degraded marble was obtained from a nearby site to act as the surrogate for the marble in the cloister. A number of well-known consolidants was used in the study: nanolime (*CaLoSil E-15*), ammonium oxalate (*ad hoc* formulation), ammonium tartrate (*HCT*), and a group of alkoxysilane consolidants – *FUNCOSIL 300*, *HCT + FUNCOSIL 300*, *FUNCOSIL 300E*, and *FUNCOSIL 300HV*. *FUNCOSIL 300* typically deposits approximately 30% silica from the initial liquid. *FUNCOSIL 300E* is an elastified version of *300* that is designed to reduce cracking of the gel both in curing and in field performance, and, *FUNCOSIL 300HV* contains an alkoxysilane coupling agent specifically designed to bond to carbonate minerals such as calcite. After treatment, samples were subjected to a hot temperature cycling using a QUV environmental chamber (4 hours condensation at 50 °C and 4 hours inactive for 10 days) and performance was evaluated using biaxial flexure (ASTM C1499).

As can be seen in Figure 1 (load *vs.* strain graph), all of the consolidants provide strength increases to the degraded marble with the exception of the *CaLoSil E-15*, which is actually lower in strength than the untreated sample.

Figure 2 shows that after exposure in the environmental chamber, all of the consolidants that had previously provided strength increases have now lost almost all of their strengthening effect with some – *FUNCOSIL 300* and *300E* – lower than untreated and weathered samples. On the other hand, the *CaLoSil E-15* treated samples have *increased* in strength, possibly due to increased carbonation of the calcium hydroxide in the formulation.

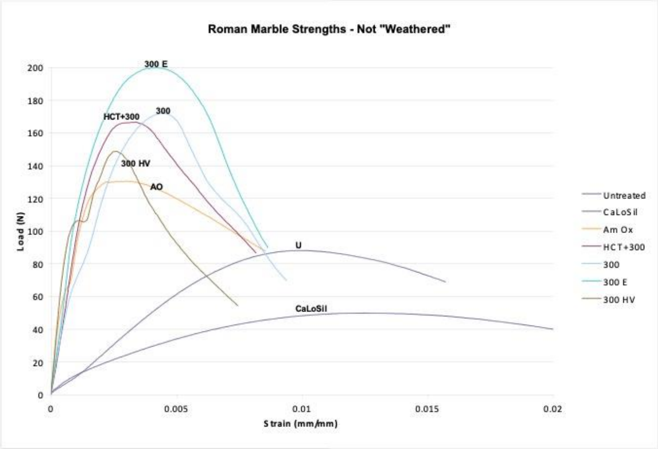

Figure 1. All consolidants with the exception of CaLoSil provided significant strength increases to the degraded marble.

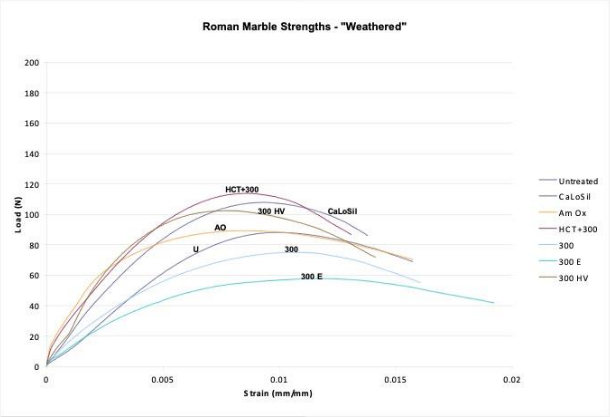

Figure 2. All consolidants with the exception of *CaLoSil* have lost much of the strength provided before weathering. The *CaLoSil* treated samples have increased in strength above the untreated and weathered samples.

As can be seen by comparing the untreated samples in Figure 1 to the untreated and weathered samples in Figure 2 the loss in strength in other samples is entirely due to the loss of performance of the consolidant. Unlike results reported elsewhere for sandstone, this marble treated with most treatments – alkoxysilanes, alkoxysilane specifically made for carbonate minerals, elastified alkoxysilanes designed for reduced cracking and resistance to mechanical weathering, and, reactive versions such as ammonium oxalate and ammonium tartrate (and a combination of ammonium tartrate and *FUNCOSIL 300*), do not retain their strength increases when exposed to a relatively mild weathering regiment while the nanolime increases in strength under the same conditions.

Consolidation of Three Berea Sandstones with Two Alkoxysilanes

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KEY-WORDS: Conservare OH100, FUNCOSIL 500 STE, alkoxysilanes, sandstone, thermal stress

The work presented here evaluates the performance of two alkoxysilane consolidants – Conservare OH100 and FUNCOSIL 500 STE – using biaxial flexure testing on three sandstones – Berea sandstone (Ohio, USA) quarried and installed in three different campaigns of building (1860, 1870, 1900) at the Parliament Building in Ottawa, Canada. Untreated and treated samples are subjected to two different environments – a hot temperature cycling and a cold temperature cycling. The three sandstones are similar in mineralogy (subangular to subrounded grains measuring between 0.06 and 0.25 mm of primarily quartz with lesser amounts of feldspars and minor kaolinite) and similar in porosity, each approximately 16-17% v/v.

Conservare OH100 and *FUNCOSIL 500 STE* differ in their formulations: *OH100* yields approximately a 30% mass return silica gel from the initial mass of liquid and *500 STE* yields approximately 50%. For *500 STE* both the initial liquid and final gel contains solid nano-particles of silica and is elastified using flexible hydrocarbon chains linked to the alkoxysilane-derived oligomers. The experimental program is designed to assess initial strength increases in consolidated samples as well as how strengths may be influenced by hot temperature and cold temperature cycling. Hot temperature cycling consisted in 60 cycles ranging from 30 °C to 55 °C and cold temperature cycling from -10 °C 22 °C. Untreated samples of each stone type were also subjected to thermal cycling.

Tables I summarizes all the results for all three sandstones. As can be seen in the table, untreated samples were largely unaffected by thermal cycling with only the 1900 samples experiencing a decrease in strength with cold cycling. Strength increases for all consolidated samples ranged from 200 to 300%. All samples treated with *Funcosil 500STE* and the 1870 and 1900 samples treated with *Conservare OH100* exhibited similar strength increases that were largely unaffected by thermal cycling. A concern expressed in the literature for consolidants applied to deteriorated stone is that the elastic modulus may increase to a detrimental degree along with strength increases. As can be seen in Figure 1 (stress-strain graph for the 1860 stone treated with *Conservare OH100*), the slopes of the consolidated samples as compared to untreated samples are quite high. There is currently no standard by which to judge when an increase in stiffness may be problematic.

	Untreated	UCC	UHC	*OH 100*	*OH 100* CC	*OH 100* HC
1860	1.1	1.0	1.0	4.4	4.6	4.5
1870	1.3	1.3	1.3	4.2	3.8	4.8
1900	0.7	1.0	0.4	3.8	3.6	4.0
				500STE	*500STE CC*	*500STE HC*
1860				4.5	4.0	4.0
1870				4.4	4.5	4.2
1900				3.6	3.6	3.6

Table I. Biaxial flexure strength measurements for Berea sandstone samples: untreated, treated and both thermal cycled. All values are in mega Pascal (MPa). UCC = untreated and cold cycled and UHC untreated and hot cycled. CC = cold cycled and HC = hot cycled.

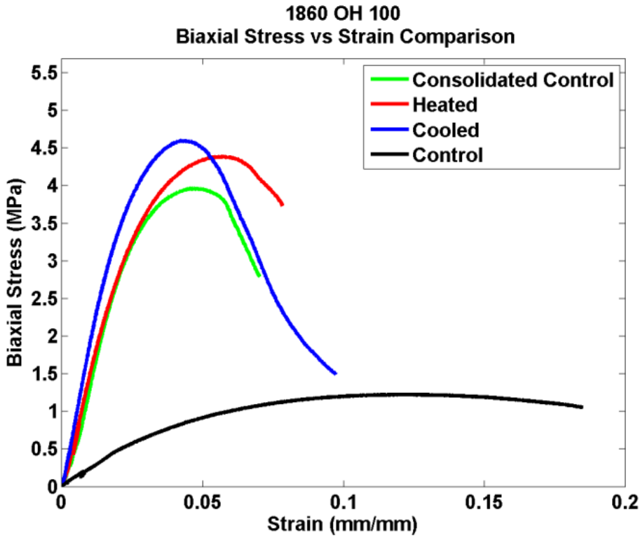

Figure 2. The stress-stain graph of the 1860 samples treated with *Conservare OH100* is typical for the three Berea sandstones. Results are similar for *500STE*. The strength increases are large and are not significantly changed by thermal cycling. In addition to large strength increases the change in elastic modulus or stiffness is also large.

In conclusion, the three quartz-rich sandstones with small amounts of kaolin clay are similar in porosity (16-17% v/v). Untreated samples are relatively weak at around 1 MPa. Untreated samples are relatively unaffected by thermal cycling but also experience significant increases in strength with both *Conservare OH100* and *Funcosil 500STE* – ranging from 3.6 to 4.8 MPa. Treated samples were also relatively unaffected by thermal cycling. Finally, on these sandstones, there is little difference in performance between *Conservare OH100* and *Funcosil 500STE* for samples that are not thermally cycled and for samples that are either cold- or hot-thermally cycled.

Di-Ammonium Phosphate for the consolidation of carbonate stone: an improved protocol

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KEY-WORDS: di-ammonium phosphate, carbonate stones, consolidation, porosity, DAP

Consolidation of stone artefacts is a complex intervention often difficult to resolve for monuments made of porous stone materials, affected by soluble salts and exposed to the weather. When dealing with calcium carbonate-based artefacts, the situation is even more critical due to intrinsic vulnerability to acid rain and condensation.

Consolidation is an irreversible intervention and therefore it is fundamental to select materials and methods durable and compatible with the substrate. In addition, retreatability is an important aspect considering that outdoor monument will need further intervention.

In the last decades, many research groups in Italy and elsewhere have obtained important results for carbonate stone using ammonium oxalate as a passivating agent and di-ammonium phosphate (DAP) for their consolidation. Particularly, DAP showed to be a very promising consolidating treatment as it matches the desired conservation requirements for carbonate stone lithotypes (Matteini et al. - 2011). DAP solubility, non-toxicity and ability to form stable and compatible products with calcium carbonate substrates (i.e. limestone) are among the most important advantages.

Work is ongoing on the application parameters, such as concentration of DAP and sequence of applications. These factors, particularly the concentration of DAP solution, seems to play an important role on the final consolidation effect, in particular on consolidation efficacy and depth of penetration. A number of case studies have shown significant improvements when DAP is applied in two steps: first as a diluted solution and then as a more concentrate one. These studies show the advantage of the two-steps applications on Carrara marble's monuments (Bordi et al. - 2020) while the research presented here focuses on the two-step application on two different carbonate stones largely used for architectural monuments in Italy: Lecce stone and Finale stone. These two types of stone have very different porosity.

In this study, DAP was applied in two-steps on 5x5x2 cm samples (on triplicate) of these two types (Fig. 1) of stone with the following procedure:

Step 1: 0.5 % DAP solution applied by poultice for 24 h.

Step 2: 4 % DAP solution applied by poultice for 24 h.

Fig. 1. Treated samples. The image shows the stone samples during the application of DAP. In particular, the upper raw shows the Finale stone samples with the poultice.

The amount of material deposited was assessed gravimetrically (one week after DAP application) and showed that less than 1% of material was added in the stone blocks.

One month after the application, the effect of DAP treatment was evaluated by instrumental analyses and physical methods:

- Water Capillary Absorption (WCA), measured up to 96 hours (following standard EN 15801: 2010, – Conservation of Cultural Properties – Test methods – Determination of water absorption by capillarity), which corresponds to a constant exposure of the samples to water for four days, showed, as expected, that WAC was reduced following DAP consolidation. Lecce stone, being much more porous, absorbs 10 times more water than Finale stone. Similarly, the kinetics of water uptake is higher for Lecce stone both treated and untreated. Capillary Absorption Coefficient (in $g/cm^2 \cdot s^{1/2}$), calculated as the angular coefficient of the first part of the curves, (i. e. the initial rate of water absorption) in the samples treated with DAP is lower (Lecce stone: $5 \cdot 10^{-4}$ vs Finale stone: $1 \cdot 10^{-4}$) than that of the untreated stones (Lecce stone: $4 \cdot 10^{-3}$ vs Finale stone: $3 \cdot 10^{-4}$).

- The Drying Test (following standard Normal Test 29/88, CNR-ICR Ed, Roma, 1991) shows that both treated and untreated samples complete the release of water at the same time (4 days).

- Portable XRF analysis confirmed the presence of phosphate close to the surface of treated samples, while at 5 mm depth of a cross-section no phosphorus was identified.

- Scanning Electronic Microscopy (SEM) was used to visualize the element phosphorous in stone specimens mounted in cross section. The objective was to identify the presence of phosphorus and visualize it, with elemental mapping, to evaluate the depth reached by the consolidating reagent DAP. SEM allowed the identification of phosphorus but at very low concentration/counts and limited to the surface layers, slightly higher in the Lecce Stone specimens as compared to the Finale Stone. In the future, the study of these cross sections in search for phosphate will be carried out with Raman spectroscopy and/or with FTIR spectroscopy.

- A recently developed Planar Abrasion Meter (PAM) was used to measure the coefficient of abrasion resistance as a function of depth (PAM is described in Sikorowski et al. - 2020). The untreated stones show constant values of abrasion resistance over the entire thickness investigated; Finale stone values are about an order of magnitude higher than those obtained for the Lecce stone. As for the consolidated stones, the results show that the DAP treatment increased abrasion resistance in both cases, but in different ways. In the case of the Lecce stone, the resistance is double in the outermost layers and decreases, reaching, at about 0.1 cm depth, constant values close to those of the untreated stone. In the case of the Finale stone, the abrasion resistance trends are not very reproducible or easy to interpret, probably because of the heterogeneity of the stone itself; however, even in this case there is greater resistance to abrasion of the treated stone compared to the untreated ones.

Considering some positive experiences found in other circumstances for monuments already treated in recent years with the 2-step DAP procedure, now supported by the promising results obtained in the current research, important monuments in the Ligurian area, made up of limestone, have been treated with the 2-step DAP protocol under the supervision of the Superintendency of Genoa. A specific study is now underway on samples taken from the monuments treated, before and after the DAP treatment, to verify the formation of new consolidating phosphate phases and evaluate their penetration into the stone.

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Exemplary conservation of the St. Salvator rock chapels in Schwäbisch Gmünd – Lessons learned and results of monitoring after consolidation

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KEY-WORDS: Moisture-resistant stone consolidation, TEOS, micro-emulsion, monitoring

1 INTRODUCTION

From 1617 to 1621, the natural rock church above Schwäbisch Gmünd was enlarged by Kaspar Vogt with an upper and lower chapel, known as St. Salvator. The wall surfaces in the upper rock chapel show a figurative relief from the life of Christ – a Mount of Olives representation, completed in 1620. This piece of art, singular in Germany, is worked out directly from the rock slope, consisting of Stubensandstein of the middle Keuper. The natural, permanently moist environment of the rock has led to severe deterioration in form of a strong grain connection loss. Black incrustations have developed on several parts with zones of underlying disaggregation and microbiological infestation. A progressive loss of the original surfaces has evolved and a conservation treatment was inevitable (Fig. 1). Due to the natural, high moisture with seasonal fluctuations, no existing consolidation product or procedure was suitable to stabilize the object. Drying of the relief was no alternative, because its condition was too fragile and a loss of material would occur. These preconditions defined the focus for the research project from 2010 to 2015 lead by University of Stuttgart to develop a stone consolidation product suitable for moist objects and to conserve the two rock chapels in an exemplary way (Frick and Zöldföldi 2015). The upper chapel was treated 2015 and the lower one in 2016 followed by an extensive monitoring.

Fig.1: Details from previous state: Crusts and loss of material, decomposition and SEM image of a fragment with biogenic cover mixed with salt crystals.

2 RESULTS AND DISCUSSION

The consolidation of heavily moistened stone by commercial ethyl silicate products is a risky procedure, since the presence of ambient water frequently leads to a rapid gel formation on the stone surface, thus preventing the further intrusion of the strengthener. Specially designed micro-emulsions of the o/w-type have been tested in the laboratory, followed by application tests in situ. With the help of drill resistance as well as ultrasonic velocity measurements it could be demonstrated that these products are able to be transported inside a moistened stone structure up to a pore size filling with water of some 50 %. Since the micellar particles have a larger size than an ethyl silicate molecule, a sufficient intrusion depth is only possible in the case of coarse grained sandstones.

The consolidation started with a laser cleaning followed by an mechanical removal of biogenic cover at infected spots. The consolidant was intrused by a first floating followed by smaller amounts with syringes. A consolidation depth of up to 20 mm was reached. Mould growth at certain spots and salt mobilisation after the treatment could be easily removed (Fig. 2).

Fig. 2: Conserved Mount of Olives representaion.

Acknowledgement

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Base-catalysed alkoxysilanes for carbonate stone consolidation

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KEY-WORDS: alkoxysilanes, basic catalysis, consolidation, carbonate stones, built heritage

INTRODUCTION

Alkoxysilanes, particularly tetraethoxysilane-based (TEOS) formulations, have long been applied in the consolidation of historic stone materials. However, sol-gel reactions of several of these formulations can be potentially influenced by high-pH environment within the pores of carbonate stones, which are the stones of election in built heritage. Those stones reduce the catalytic activity of most common catalysts (acid or neutral *e.g.* (Mosquera et al. 2008; Salazar-Hernández et al. 2009) and can modify sol-gel paths in a way that silicate structures with poor capacity to provide cohesion to stone are produced (Sena da Fonseca et al. 2019) . Therefore, the alternative use of a base-catalysed product appears an obvious and viable choice, something that has not yet been properly explored until recently by the authors' (Rodrigues *et al.* 2021).

EXPERIMENTAL

The development of new base-catalysed sols for the consolidation of carbonate-based stone was achieved in this work by tuning several sol-gel parameters (*e.g.* TEOS-solvent ratio and TEOS-catalyst ratio). Four different basic catalysts with different basicities (ammonia and three alkanolamines: octylamine, diethanolamine, and triethanolamine) were used together with TEOS, ethanol and water (at different ratios) to produce sols and assess their potential to act as consolidants. Xerogels obtained from sol-gel synthesis within flasks were analysed. Calcite powder and limestone samples were treated with sols.

RESULTS AND DISCUSSION

Both highly cracked and a small group of monolithic xerogels were achieved. The microstructure of xerogels was found to be mainly dependent on the basic catalyst, and it varied from well-connected silica nano-spheres to flocculated porous materials. The most promising sols were prepared with the use of ammonia and triethanolamine as basic catalysts. Even if some of the base-catalysed sols developed unfavourable microstructures for a potential efficient consolidation, there were cohesive monoliths of calcite powder and significant and homogeneous drilling resistance(DR) increments caused by a selection of sols. The improved sols considered as presenting potential 'effectiveness' through uniform increment of DR in-depth, within the limits defined in the literature (Delgado Rodrigues and Grossi, 2007) showed low potential of formation of hardened superficial layers and colour alteration, *i.e.* 'harmfulness'.

CONCLUSIONS

The significant and uniform drilling resistance increments and the lack of significant colour variation of stone specimens upon treatment with a selection of sols confirmed the potential of using base-catalysed alkoxysilanes as consolidation products for carbonate stone.

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Carbonate stone consolidation with tailored alkoxysilanes with poly(ethylene glycol)

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KEY-WORDS: alkoxysilanes, PEG, consolidation, carbonate stones, built heritage

INTRODUCTION

The existing commercial solutions and the efforts to produce tetraethoxysilane (TEOS)-based products to consolidate carbonate-based stones are still considered unsatisfactory. Drawbacks such as the influence of the carbonate media and the tendency of the gel to crack during the drying-shrinking phase are well-known (Sena da Fonseca *et al.* 2018). Several authors have used modified alkoxysilane formulations with the addition of flexible polymeric chains to overcome the cracking tendency – *e.g.* (Salazar-Hernández et al. 2010). However, the ongoing research towards more advanced solutions emphasises the need to achieve more satisfactory results. The non-hydrophobic poly(ethylene glycol) (PEG), already employed in other applications showing potential to play a multifunctional role in the process of gel formation (Xiang et al. 2017) , has never been successfully applied for stone consolidation purposes until the authors' recent advances (Sena da Fonseca *et al.* 2016, Rodrigues *et al.* 2021). Thus, following the most recent results, this work addresses the development of new TEOS-based solutions for the consolidation of limestone using PEG as an organic modifier, using both acid and basic catalysts.

EXPERIMENTAL

Sols were prepared using TEOS as silica precursor, ethanol, water, PEG (in distinct amounts) and 3 catalysts (HCl; n-octylamine and diethanolamine). Xerogels within inert flasks and treated calcite powder and limestone samples were used to evaluate the viability of the formulated sols. Validation of the most promising sols was performed on limestone samples.

RESULTS AND DISCUSSION

Sols formulated without or with the lowest amounts of PEG lead to cracked xerogels (independently of the used catalyst). When PEG was added, the cracking degree decreased. Calcite blends' cohesion also increased with the increase in PEG content, in particular in HCl and Oct catalysed sols with two different TEOS:solvent ratios. When treated with the latest sols, several stone samples showed an increase in their drilling resistance upon treatment.

CONCLUSIONS

The results demonstrate that: (i) less cracked xerogels were obtained with the incorporation of PEG either under acid or basic catalysis; (ii) sols with the capacity to provide cohesion to calcite powder were obtained; (iii) viable sols for application into stone substrates were achieved with the addition of PEG either under acid or basic catalysis and (iv) there was an effective improvement of the cohesion of the carbonate stone specimens tested.

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

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

Introduction

Numerous stone-built heritage monuments around the world have been consolidated to prolong their life span, and assessing the long-term performance of such treatments remains challenging. Building stones exposed outdoor may take decades to respond to the environment through degradation and weathering, 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 conducted so far. In long-term weathering, the variability of the environment combined with accumulated weathering stress over time, causes complex stone responses. Multiple mechanisms like crust forming and surface recession compete, resulting in non-linear behaviour that is difficult to predict. Nevertheless, the few well-documented long-term outdoor exposure trials provide invaluable insights into the performance of stone consolidants over time, because they account for both accumulated weathering history and environment variability. One such example is the ‘Stone Deterioration and Stone Conservation’ project, a former large-scale interdisciplinary exposure trial funded by the Ministry for Research and Technology in Germany (BMFT, now BMBF) in 1986-1996. For more than 30 years, large specimens known as 'Asterixe,' with complex geometries that mimic architectural characteristics, have been exposed to known outdoor environmental conditions. This unique archive and scientific resource 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.

In November 1995, after about 10 years of outdoor exposure in an Alpine climate in Holzkirchen (Germany), two consolidants were applied to five Ihrlersteiner (a green to green-brown, fossiliferous sandstone) Asterixe specimens, a hydrophobic silane modified polyurethane prepolymer and a non-hydrophobic epoxy based resin. The latter (as one of the few remaining treated specimen) is the objective of this study which aims to compare the data collected in 1995 with that collected in 2019, focusing on three Asterixe, two not treated and a consolidated one.

In 1995, the Asterixe were cleaned and both Ultrasonic Pulse Velocity (surface) and water uptake (Karsten tube Ø 50 mm) were measured before and after the consolidation treatment. Yet, whether the UPV measurement was made parallel or perpendicular to the bedding is unknown; a crucial information for a stone type with a high level of anisotropy like the Ihrlersteiner. Further, the only archival information we have on the historically used transducers is that they covered a frequency spectrum of 50–150 kHz and were designed specifically for dry coupling. For the 2019 study, the Pundit Lab(+) Proceq© with exponential transducers (54kHz) and an elastomer as couplant was used to produce 2D tomograms for planes at two different heights in unsheltered and sheltered areas, with the p-wave 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). In agreement with the literature, this study observed differential erosion (rounding and roughening), granular disintegration, fragmentation and biocolonisation on all specimens, and crack formation on the consolidated one. Overall, the material characteristics have become more heterogenous and all follow a similar trend of differential weathering according to the main weathering direction (South-West).

The on-site approach was complemented with a laboratory study on a weathered Ihrlersteiner specimen correlating the direct and the indirect UPV method, to arrive at a proxy comparison for the historic and the recent study data. A multistep procedure of data conversion was pursued as both different types of UPV transducers and application methods are not directly comparable. We experimentally defined a conversion factor of 1.22 for exponential transducers (5mm diameter, 54 kHz) to standard transducers (50 mm diameter, 54k Hz) and 1.49 for the direct to the indirect method. However, when we apply the conversion factors to the data, we get considerably higher V_p than the historic V_p and also as is generally reported for fresh Ihrlersteiner sandstone. 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 of the exposed Asterixe. Moreover, the inherent variability of the tested stones, which increases with extended exposure, adds further uncertainty and cannot be disregarded. To reduce the uncertainty and ensure the value of this long-term exposure trial beyond its more realistic presentation of real-world stone weathering behaviour it is planned to complement the non-destructive characterization and perform laboratory investigation on collected samples.

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

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INTRODUCTION

Crac Des Chevaliers is a remarkable medieval fortress in Syria. It is a combination of Crusader and Islamic architecture leftover since the 12th-13th century (Mesqui-2018). This unique structure suffers from serious issues that need urgent intervention. The castle is in a rural area whose summers are dry and have mild-wet winters. 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; decay types (Török and Rozgonyi-2004), salt crystallisation (Pápay et al.-2021) and biological colonisation on the stone surface as well (Bilal and Rozgonyi 2020).

RESULTS AND DISCUSSION

The most serious issues at the castle can be defined as: (i) damaged stone blocks due to the recent armed conflict in Syria. (ii)The growth of invasive plants, especially the presence of shrubs that threaten the stability of the whole wall. (iii) The castle represents a favourable environment of the flourishing of various species micro-organisms' colonisation that are widespread at the castle. (iv) Salt crystallisation. (v) The discoloration with the orange of both eastern and southern façades

Deterioration mapping

Two deterioration maps were carried out to a building in the castle with different directions: 107 m^2 northern external façade and 175 m^2 eastern external façade. Deterioration mapping revealed that the orientation and location of stone blocks influence the type of stone deterioration at the castle. The external facades with the same direction are distinguished by the same stone decay types that distribute at the façade in varying percentages.

Schmidt hammer rebound test

Schmidt hammer results revealed that the castle was constructed from a variety of lithotypes. A set of stones was tested, each with a unique location, condition, and a specific deterioration type that exhibited a range of rebound values

Rilem tube penetration test

The results presented different kinds of absorption behaviour of stone blocks. The investigation showed that it depends on both the condition of the stone, i.e., stone deterioration type, its spread, how the intensity of it on the surface, and the orientation of the stone (Figure 1).

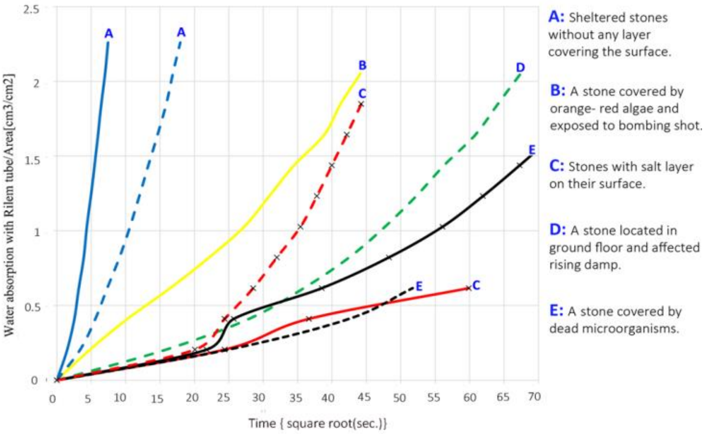

Figure 1 The absorption diagram of the tested stones by Rilem Tube

Conclusion

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 enhancement of absorption rate when the water pressure can dissolve the salt layer on the surface, facilitating the passage of water inward. That ability is most probably related to the thickness of the salt layer as well as the type of the salt itself. On the other hand, the stones covering by microorganisms showed relatively low to no-absorption behaviour where the layer of microorganisms highly affected the wettability property of the stone.

The use of a Schmidt hammer in the castle revealed that the castle stones belong to various lithotypes, which reflect a range of rebound values. It is also well demonstrated that the rebound values of eroded surfaces, damaged stones, and stones exposed to water infiltration were relatively low.

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Behaviour of consolidation treatments applied on a soft limestone after natural exposure under a marine environment

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KEY-WORDS: Soft limestone; consolidation; natural exposure, marine environment.

INTRODUCTION

The weathering of soft porous limestones frequently leads to severe damage and, in these situations, consolidation has been practiced by using various products to avoid the replacement of stone blocks. Although it is recognized the risk of consolidation treatments the research has been focused on the development of new products rather than on studying the frequent cases of poor long-term effectiveness and, worst than this, the short-term and delayed harmfulness of the applied treatments.

The present study analyses the potential long-term effectiveness and delayed harmfulness of consolidation treatments exposed to a marine environment for about 4 years. The tested treatments were carried out with commercial consolidants frequently used in the past at European level, in cultural heritage stone objects on a very soft limestone with 27% of porosity (Ançã stone). Detailed information can be found elsewhere (Ferreira Pinto, 2002), (Perdiz, 2016).

MATERIALS AND METHODS

Stone slabs with a surface area of 160-280 cm^2 and a thickness of 2.5 cm were used as specimens and treated, until saturation, by brushing with 3 consolidants: ethyl silicate (Tegovakon), acrylic resin (Paraloid B72) and a cycloaliphatic epoxy resin (EP 2101). A non-treated area was kept in all specimens. The treatments were assessed after treatment, and monitored after 16 months and 4 years of exposure through visual observation, the evaluation of drilling resistance (DRMS), superficial hardness, water absorption and color. It is worth mention that DRMS identified the increment of the initial resistance due to the treatments in almost all thickness of the tested specimens.

During natural exposure the specimens were mounted on a steel structure, located in “Cabo da Roca”, positioned 45º to the horizontal and facing west in order to enhance the exposure to the sea spray. “Cabo da Roca” is a promontory in the Portuguese Atlantic west coast located 50 km west of Lisbon (Portugal) at an altitude of 140m.

RESULTS AND DISCUSSION

After exposure, all untreated areas of the Ançã specimens revealed signs of decay that started to be present at the end of the 1 year of exposure. Superficial roughness, powdering and reduction of the superficial hardness were the identified signs of decay on the untreated stone areas of the stone specimens.

After 4 years of exposure, the surface treated with ethyl silicate registered visual signs of surface degradation and reduction of superficial hardness, while those treated with the epoxy and acrylic resins revealed an increment of their superficial hardness and a stable condition, following what was identified after 1 year. Regarding the in depth resistance of the treatments, DRMS did not identify relevant alterations.

During the monitoring period, it was also registered the increase of water absorption capacity of all treatments and reduction of the colour variation initially promoted by the ethyl silicate and epoxy treatments, while the color variation triggered by the acrylic resin became more relevant after 4 years than initially.

In summary, the obtained results point out that the potential long-term effectiveness of the consolidation action of the tested treatment is almost stable after the 4 years of exposure and no relevant delayed harmfulness was identified.

CONCLUSIONS

Even though the exposure tests under natural environments are usually considered as being able to better reproduce real conditions than artificial aging tests, it is important to be aware that they do not reproduce the diversity and complexity of the reality, since the initial and long-term behaviour of the treatments depend on diverse factors at different levels, such as decay agents~~,~~ dimension and shape of the real objects, conditions of exposure of the surfaces and the circulation of water into masonry elements, among others. Thus, the obtained results should be carefully considered, especially when used in practice to support decision processes of selection treatments for decayed objects of cultural significance, since they were obtained on sound specimens almost totally consolidated, which does not reproduce the large majority of onsite treatment conditions, nor the diversity of the existing environments.

AKNOWLEDGMENTS

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Conservation of the 16th C. Pietra Serena sandstone elements of the Loggia at Villa Rucellai (Prato, Italy)

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KEY-WORDS: Consolidation, Pietra Serena, fluosilicate, sandstone, ethyl silicate.

INTRODUCTION

Villa Rucellai is an historical residence dating back to medieval time and situated near Prato (Florence, Italy) (https://www.villarucellai.com/en/history.html). Following early architectural variations, it reached its current appearance in the 16th C. with the inclusion of the Renaissance facade flanked, on the west, by a loggia. This extended abstract focuses on the conservation of the *Pietra Serena* elements of the Tuscan loggia: three columns and a horizontal coping. *Pietra Serena* is a gray sandstone particularly used in historical Tuscan architecture for isolated or decorative elements such as columns, cornices and ribs. This type of stone comes from the northern part of the Apennines and is composed of metamorphic and granitic rocks clasts in a matrix of clay minerals (Amoroso 2002, Malesani et al. 2003, Malesani et al. 1974). The *Pietra Serena* elements give the Villa a distinctive character, but also conservation problems due to the nature of the stone and their external exposure. Natural physical-chemical processes, mostly related to temperature and humidity changes, are the main cause of this stone's decay which is manifested by the formation and loss of crusts parallel to the external surface (exfoliation), pulverization, detachments, and cracks. There is only few historical information on the loggia's conservation history starting from its construction, restoration and conservation. In 1973, the stone of the loggia was treated using fluosilicates, a solution of magnesium and zinc fluosilicate, applied by poulticing and left in contact with the stone until complete imbibition. (Giusti *et al.*2000, Matteini *et al.* 1994). Although there is no technical information of this specific intervention, the photographs of the treatment show the columns fully enveloped, large barrels mounted up high and a system of tubing feeding by gravity the wrapped stone. Lack of maintenance possibly combined with the effect of this treatment and other physical factors, led over time to the formation of a hard and compact surface crust on the *Pietra Serena* elements. Almost 50 years later, the stone presented serious phenomena of disaggregation and delamination between and therefore, in June 2020, a conservation treatment was planned and implemented to stabilize and slow down deterioration.

MATERIAL AND METHODS

The intervention was developed based on testing, visual and analytical investigation of the stone using technical photography, FT-IR spectrometry and thin section observations. A structural evaluation of the bearing capacity of the deteriorated columns, carried out by a structural engineer, confirmed that replacement was not necessary and that the conservation could 'simply' focus on the surface of the column.

Villa Rucellai, south facade of the house, on the left is the loggia.

Pre-consolidation with ethyl silicate (Wacker_OH) applied by syringe.

INTERVENTION

The intervention included biocide treatment and consolidation with ethyl silicate (Wacker-OH) selected for its efficacy and its compatibility with the silicate nature of the stone. All water entries, cracks and losses were filled with lime mortar or dispersed-colloidal silica selected accordingly to the size of the area/volume to be filled. Larger spaces required lime-based mortar while smaller cracks could be rapidly and effectively closed using dispersed-colloidal silica (Syton® W30). The areas affected by delamination and by a dense network of cracks were filled and stabilized with lime-based injection grouts. The intervention proved to be fundamental to reduce the cycle and process of progressive decay of the affected architectural elements.

MONITORING AND MAINTENANCE

The main factors leading to stone deterioration are water imbibition and thermal fluctuations, both impossible to eliminate since the loggia is directly exposed to rain and sun. The post-treatment monitoring and maintenance program for the stone elements includes the periodic control to identify the first signs of deterioration, such as fissure or crack opening. The maintenance would include the treatment of these opening to close them and stop water infiltration. The causes of stone deterioration are intrinsic to the stone itself and the environmental conditions in which it is set and therefore cannot be eliminated. Regular control is the only solution to reduce deterioration.

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Effect of consolidation on mechanical properties of oolitic limestone

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

INTRODUCTION

Consolidation of porous stones is a common practice in heritage structure remediation. The present study focuses on the mechanical changes caused by the consolidation of a highly porous Miocene limestone of Hungary. Emblematic monuments of Budapest were built from this low strength porous limestone. These historic buildings now show severe signs of deterioration (Török and Rozgonyi-2004), and besides their visual appearance, the stone structures lost their strength. Weathered stones are often treated with stone consolidants on-site during restoration works in order to strengthen the inner structure and to provide better mechanical parameters (Pápay et al.-2021). In the present study, oolitic medium-grained limestone type from Sóskút (Hungary) was treated with ethyl-silicate (Remmers KSE 100). The porous limestone of Hungary presents a great variety in fabric characteristics (Rozgonyi-2002). The studied lithotype has millimetre-sized macropores and oolitic grainstone fabric; the average apparent porosity of 27V% and a bulk density of 1.68 g/cm3. Samples were treated in the laboratory under atmospheric pressure by full immersion in consolidant for 90 min. After 90 days curing 1.5 and 1.9 w/w% KSE 100 were found in the pores of the specimens. Mechanical parameters such as compressive strength (UCS), static and dynamic modulus of elasticity (E_{stat}, E_{dyn}), static and dynamic Poisson's ratio (ν_{stat}, ν_{dyn}) and indirect tensile strength (ITS) were measured on reference and consolidated samples.

RESULTS AND DISCUSSION

Static elastic modulus (E_{stat}) and Poisson's ratio ($\nu_{stat,}$) were determined from the linear (elastic) section of the uniaxial compressive stress–axial strain diagram. Dynamic elastic modulus (E_{dyn}) and Poisson's ratio (ν_{dyn}) were calculated based on two methods. At first, it was obtained from the velocity of longitudinal and transversal ultrasonic waves (measured with UP-SW transducers at a frequency of 80 kHz without coupling material and evaluated with LightHouse Software produced from Geotron). The second method of how E_{dyn} was assessed is using a simplified equation containing the longitudinal ultrasonic wave velocity and bulk density.

The results show that both the uniaxial compressive strength and the indirect tensile strength increased significantly after the treatment with tetraethyl silicate. Due to the treatment, the slope of the stress-strain curves increased simultaneously as the deformability decreases. As a consequence, the static modulus of elasticity increased, and the Poisson ratio decreased after consolidation. 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 in both cases.

Consequently, consolidation with KSE 100 on porous limestone caused a significant change in the mechanical parameters. Compressive strength (+62%), static modulus of elasticity (+81%), dynamic modulus of elasticity (+35%) and tensile strength (+61%) increased; however Poisson ratio decreased with 17% after consolidation (Figure 1).

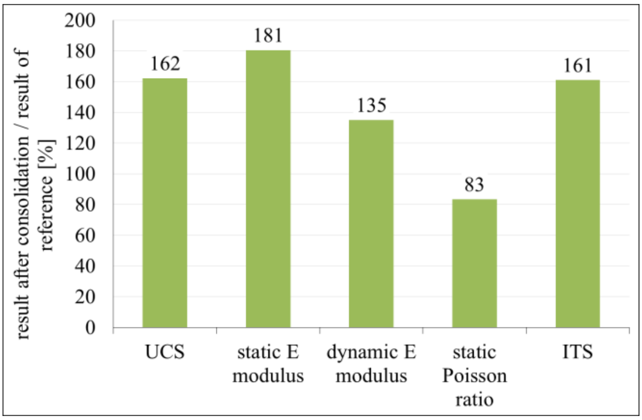

Figure 1 Change in UCS, static modulus of elasticity, dynamic modulus of elasticity, static Poisson ratio and ITS after consolidation

The deformability of the porous limestone decreased, and the rigidity increased due to consolidation. The ratio of dynamic and static modulus of elasticity grew after consolidation, and it was much higher than other results reported in former literature (Mockovciaková and Pandula-2003). This phenomenon is caused by the very weak structure of the investigated lithotype with its high porosity, very low bulk density and the presence of macropores.

Our study indicates that consolidation leads to an increase in strength; however, the increase in strength alone does not justify the consolidation since other properties such as porosity or water absorption are also critical parameters when the compatibility issues of such intervention are judged.

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

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Extended abstract

It is of common understanding that the scientific message, to fulfil its purpose, must be 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.

Studies on consolidation treatments are carried out under distinct contexts and perspectives aiming 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.

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.

The full paper of this abstract can be found in the proceedings of this same symposium (Delgado Rodrigues 2021a). Complementary information on this theme can be found elsewhere (Delgado Rodrigues and Ferreira Pinto 2019), (Delgado Rodrigues 2021b), (Delgado Rodrigues and Charola 2021).

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

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The earliest use of alkoxysilane for stone consolidation in Austria: The classical case of a harmful effect

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KEY-WORDS: over-consolidation, mechanical strength, treatment performance, hydrophobic treatment, sandstone.

INTRODUCTION

Stone consolidants need to fulfil a range of criteria of compatibility and efficiency when they get applied on monumental surfaces. Nevertheless, in some cases a treatment may also cause harmful effects, worst of which result in spalling of the treated surface. The present study evaluates the first Austrian alkoxysilane consolidation applied on a siliceous sandstone type, used for the construction of the Romanesque Charnel House in Tulln, Lower Austria. Conservation treatments as a two-component system based on TEOS with an additional hydrophobic effect had been repeatedly applied since the 1970s aimed at providing a strengthening effect and water repellence.

ANALYTICAL AND PHYSICAL METHODS

In order to evaluate the state of these historical treatments, four drilled cores were extracted and analysed by means of ultrasound pulse velocity, splitting tensile strength, optical light- and scanning electron microscopy, ion chromatography, and water absorption.

RESULTS AND DISCUSSION

The results reveal an over-consolidation of the stone up to a depth of 2 to 5 cm, detected by a depth profile analysis using ultrasound pulse velocity and splitting tensile strength (Figure 1). Thereby, the maximal allowed threshold for mechanical strength gradients between treated and untreated stone according to [1] proved exceeded. Microscopic investigations confirmed the presence of at least two silica gel generations indicating different consolidation campaigns. Furthermore, the distribution of gypsum in the porosity suggests that part of this damaging salt was crystallized after and/or between the consolidation treatments and might have contributed to the detected over-consolidation and subsequent damages of the surface. Both, the mechanical properties of the over-consolidated zone and the appearance of the consolidant in the pores indicate an efficient state of conservation several decades after the treatment. However, the untreated stone behind the over consolidated zone is the reason for the poor treatment performance. Ion chromatography revealed the presence of sodium chloride, gypsum and nitrate salts in low concentrations (<0.5 w/w%). The water-related tests indicate a hydro repellent treatment hindering moisture transport through the affected layers even after approx. 40 years of outdoor exposure.

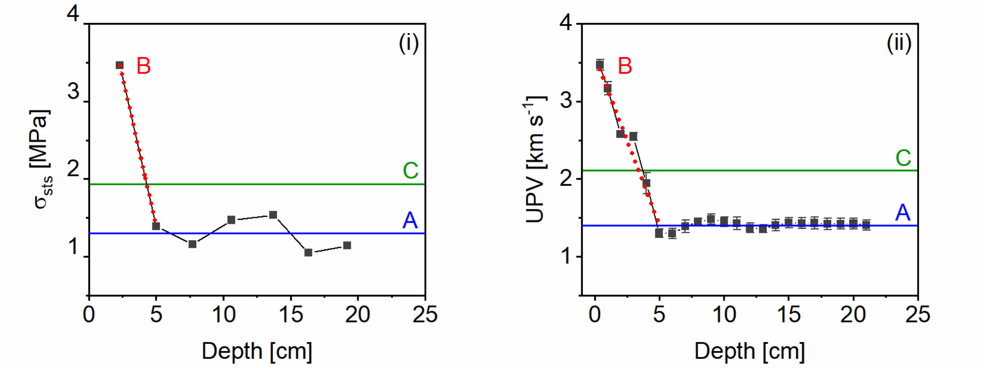

Figure 1. Depth profiles of one drilled core measured by means of **(i)** splitting tensile strength and **(ii)** ultrasound pulse velocity; in the untreated areas (A) against the treated surface layers (B); the maximal difference recommended between treated and untreated layers according to [1] is indicated by (C).

The results of such a conservation treatment seemingly left little choice but to wait for damage to develop and then act locally by sealing the façade (i.e. restoring the hydrophobic barrier and backfilling of contour scaling). We argue that a consolidant reaching a lower increase in mechanical strength would have possibly been more advantageous, as the difference between treated and untreated layers would be lower. Moreover, the durability and ageing are not the same for the consolidated and water-protected layers as opposed to untreated layers. Comparison of ageing of consolidated, hydrophobic and, untreated substrates is lacking in research to reveal future scenarios.

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Identification and Documentation of Deterioration Patterns in Portuguese Limestones Applied in Brazil and Portugal

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KEY-WORDS: Lioz, Heritage, Deterioration

From the collection of stones applied in Cultural Heritage elements in Brazil and Portugal, materials of limestone composition stand out. Among them, there are varieties generically referred to as *Lioz*, which correspond to the most applied ones in both countries.

In Portugal and Brazil, examples of constructions with applications of different types of *Lioz* limestones (*Lioz*, *Chainette*, *Encarnadão*, *Amarelo de Negrais*) are abundant. Regarding the Portuguese case, the period of their constructions covers an extensive time interval, encompassing the 20th century, as in the cases of coatings in Lisbon subway stations and in the construction of the Belém Cultural Center in 1992, where varieties of *Lioz* were more frequently used – more specifically those identified as *Lioz Abancado*, also known as *Lioz* of Pero Pinheiro. In the Brazilian case, the oldest applications date back to the 18th century, despite also reaching the 20th with rare examples of internal coatings of yellowish, reddish and whitish *Lioz* varieties, as in the case of the Museum of Modern Art of Belo Horizonte, from 1943, and the 1947 Gustavo Capanema Palace, located in the city of Rio de Janeiro.

From the set of important Portuguese monuments, some of the oldest, such as the Cathedral of Lisbon (built from the 12th century and partly with the use of clear *Lioz* limestones) present a construction history of many centuries, whereas others, such as the Jerónimos Monastery, the *Nossa Senhora de Loreto* Church, from 1518, and the Tower of Belém, from 1519, located in the region of Lisbon, had their constructions started and completed in the first years of the 16th century, and can even be considered contemporary with most part of the Brazilian history. The Jerónimos Monastery, for example, whose construction started around the year of 1501, has a predominance, among its limestones, of the whitish, fossiliferous or not, sometimes with stylotites *Lioz* types. In the building, there are combinations involving types such as *Encarnadão* and *Amarelo Negrais*, but also the *Azul de Sintra*, which is not a *Lioz* type, on floor coatings or as ornamental details. Constructed later, mainly throughout the 18th and 19th centuries, Portuguese buildings such as the former *Convento de Mafra* Palace, built in the early 18th century and using limestones from the regions of Sintra and Pêro Pinheiro, such as the *Amarelo Negrais*, the *Encarnadão Chainette*, the Saint Florien Pink, the *Lióz Azulino*, but also the *Negro de Mem Martins*, which is also not a *Lioz* type; or the *Basilica da Estrela*, from 1790, which has a *façade* in *Lioz*, panels in *Amarelo Negrais* and columns in *Encarnadão*; or the *Santo Domingos* Church, with limestone columns from 1834 and the *D. Maria II* National Theater, from 1846, can be considered contemporary in relation to Brazilian buildings, in which *Lioz* was also applied. As examples of these contemporary Brazilian buildings, the following can be mentioned: the Jesuit Church of Salvador (Head Church from 1765), which has *façade* coverings in white *Lioz* and external floors in yellow, cream and red types; the *Conceição da Praia* Church, built in Salvador between 1739 and 1765 and featuring a frontispiece also in *Lioz* cream; the *São Bento* Monastery of Rio de Janeiro, built throughout the 18th century and with internal floors with beautiful compositions of different *Lioz* types; as well as the *Santa Isabel* Theater in Recife, of 1850 and with *Lioz* on the *façade* and its columns; and also the *Paço Real* of Rio de Janeiro. The *Paço* of Rio de Janeiro, which was the seat of government and residence of the Rio de Janeiro Captaincy governor between 1743 and 1763, and of the Viceroys of Brazil until March 8, 1808, has, in addition to structural blocks and applications of *Lioz* ornamentals, yellowish, reddish and grayish varieties, which were used to coat their floors.

Outcropping in the region of Lisbon, these limestones were historically applied in buildings of this city and, certainly, it was from there that they were transported for applications in Brazil. Extracted in old quarries, in the District of Lisbon, Council of Sintra (Aires Barros, 2001) and involving the sites of Pêro Martins, Negrais and Sintra, these limestones are considered to result from geological processes which date back to the Cretaceous (Casal Moura & Carvalho, 2007; Lopes, 2015). In general, they can be identified as microcrystalline, and characterized as very compact, with relatively low porosity. Calcitic in composition, though with some content of clay minerals, a part of them is characterized by the presence of rudist fossils (Fig. 01). In general, all these limestones are calciclastic and bioclastic rocks, and may contain styliolites and be very sparitized.

Figure 01: Photographs of different types of *Lioz* limestones, presenting somatofossil contents of rudist bivalve shells in different cuts (Photo: Antônio Gilberto Costa).

Another striking feature of these limestones is the extensive chromatic variation they can present (Fig. 02), ranging from whitish tones to cream or beige (most frequent *Lioz*), sometimes pink with salmon pink venules, such as *Encarnadão de Lameiras,* or with thick elements and areas or pink lines, ranging to the red (*Encarnadão*). Some, such as the *Encarnadão Chainette*, bear a purplish hue with yellowish spots, whereas others are red with white or yellow spots, up until the golden-yellow limestone (*Amarelo Negrais*). In the case of the red variations, some present yellow-orange spots, such as the *Pedra Furada Encarnadão*. In this case, it is one which corresponds to a variation in terms of facies in relation to yellow, and whose extraction took place in the Montelavar Parish, in the Sintra Municipality and Lisbon District, in areas very close to those where the yellow type was extracted.

Figure 02: Photographs of different types of *Lioz* limestones applied in buildings in Brazil and Portugal, presenting extensive chromatic variations (Photo: Antônio Gilberto Costa).

Already exposed for long periods, and as a result of extrinsic factors such as humidity, climatic conditions and pollution, as well as intrinsic factors such as their own compositions, both in the aforementioned Portuguese and Brazilian buildings, there occur degradation degrees as a consequence of processes in these limestones, namely those of erosive character (Rodrigues, 2007). According to the nomenclature proposed by the International Council on Monuments and Sites (ICOMOS), there is an extensive loss of matrix and differential erosion, which indicates the reduction of surfaces controlled by the presence of fossil elements, carbonate resistance and the presence of secondary minerals (Vergès-Belmin *et al*. 2008). Usually applied in floor and wall coatings, indoors or outdoors, they may present, in addition to the loss of their original surface, the loss of parts due to the presence of clays, for example, as in cases of applications both in floor covering and in walls subjected to conditions of greater humidity (Costa, 2021).

In this study, historical and contemporary applications, mainly involving different types of *Lioz* were considered, aiming to evaluate the influences of processes over degradation degrees in these limestones, as in the cases, for example, of the Cathedral of Salvador (Fig. 03a) and the Jerónimos Monastery, in Lisbon (Fig. 03b).

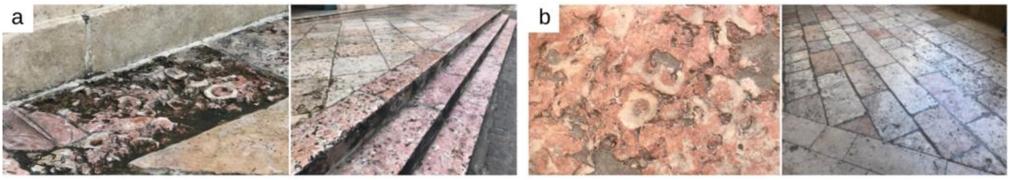

Figure 03: Photographs of the external floor of the Cathedral of Salvador, state of Bahia, Brazil (a), and of the internal floor of the Jerónimos Monastery, in Lisbon, Portugal (b). Limestone pieces presenting chromatic variation, the presence of fossils, loss of matrix and differential erosion (Photo: Antônio Gilberto Costa).

To illustrate problems involving internal applications, examples such as the internal floor and wall covering inside the *Basilica da Estrela*, in Lisbon (Fig. 04a), were considered. In another application, in Brazil, the use and degradation of the *Amarelo Negrais* limestone was considered. Applied in the 1940s decade, on internal floors of the Museum of Modern Art, in Belo Horizonte (Fig. 04b), the rock is also partly reddish or red, associated with yellow, and presents differential erosion and loss of matrix.

Figure 04: Photographs of internal floor and wall covering (right) applications of the *Lioz* inside the *Basilica da Estrela*, in Lisbon, Portugal (a), and of the internal floor of the Museum of Modern Art, in Belo Horizonte, Brazil (b). The rocks present chromatic variations, presence of fossils, differential erosion and loss of matrix (Photo: Antônio Gilberto Costa).

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Marble biomineralisation: Pilot application results at the Arch of Septimius Severus

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KEY-WORDS: Pentelic marble sugaring; biomineralisation; onsite testing; compatible consolidation; sustainable heritage conservation

INTRODUCTION

The Arch of Septimius Severus, in richly decorated Pentelic marble, was erected in the Roman Forum in 203 CE by the Senate to celebrate the victories of its namesake Emperor against the Parthians. It consists of three arches, framed by Corinthian columns with plinths featuring Roman soldiers with Parthian prisoners; the campaigns of Septimius against the Parthians are depicted above the lateral arches.

The monument's sculpted surfaces showed advanced decay, with active degradation processes inducing clear phenomena of disintegration, flaking, and fracturing, and causing the loss of considerable portions of stone material. This reality, affecting one of the most valuable monuments of the Roman Forum, required all stabilisation works to prove fully compatible with the fragility of these millennia-old marbles.

Also, this exceptional Arch sits in the Colosseum Archaeological Park, a natural setting decisively contributing to the cultural significance of its World Heritage-listed archaeological remains. Thus, the Park managing authority, Parco Archeologico del Colosseo, launched the PArCo Green project, fostering greener practices in all Park activities, including (heritage) conservation.

The compatible conservation of a work of such outstanding cultural value and the environmental and sustainability concerns of the Parco Archeologico del Colosseo were the premises upon which a bio-consolidation pilot intervention was implemented on the stone surfaces affected by problems of disintegration and pulverisation. The main goal of this study was to validate biomineralisation as a method to consolidate deteriorated marble surfaces, especially those affected by sand disintegration patterns.

PILOT

Treated area

The zone selected for biomineralisation trials comprised three planes (south, west and north) of a plinth located in the south pillar of the Arch, around 6 m^2 in area, with figurative reliefs carved in marble, still legible – significant lacunae notwithstanding –, some with grooves from the original carving tools (Fig.1).

Fig. 1: West plane of the plinth before (left) and after (right) the biomineralisation treatment.

The pilot area, like all of the Arch's surfaces, was affected by cracks, fractures, scaling, and chipping, causing instability and significant mass losses. Sand disintegration ('sugaring'), a typical deterioration pattern on exposed marble surfaces, was extensive, especially on the sculpted protruding parts. Soiling and incipient biocolonisation were also visible, as well as metal clips and mortar fills from previous interventions.

Procedures

Surface treatment

The implemented biomineralisation treatment is based on the Granada method, with a selective activation of carbonatogenic bacteria residing on the marble's deteriorated surfaces via application of a nutrient medium (Jroundi *et al*. 2010; Rodriguez-Navarro *et al.* 2015), manufactured by KBYO under the trade name Myxostone-M3P®. The effective presence of carbonatogenic strains in the Arch was analytically confirmed.

These are aerobic bacteria sensitive to ultraviolet radiation, and therefore treatment requires UV-sheltering and air circulation, achieved here by superimposing layers of common black woven plastic nets. To avoid contamination, a stringent protocol was followed to manipulate, clean, and store working tools, instruments, and containers. After initial characterisation tests, the product was applied for 8 consecutive days; the treated area remained protected for 30 days to allow process completion, after which a new set of characterisation tests was carried out. Visually, there were no colour alterations to the stone substrates (Fig.1).

Characterisation tests

Given the significance of the object, only a few methods could be considered: the peeling test, providing a direct measure of treatment-induced changes in surface cohesion; and the sponge test, which reflects treatment-induced changes in stone porosity, allowing an indirect assessment of the consolidation action.

The peeling test, following the protocol in Drdácký *et al.* (2012), was applied to surfaces without any decorative detail, with most measurements obtained on an uncarved surface left by the detachment of a large piece of stone. The sponge test, using the Pardini and Tiano (2004) method, was carried out on flat surfaces where good contact between the sponge and the stone could be achieved.

RESULTS AND DISCUSSION

Fig. 2 displays the results of the water absorption test performed in the same areas before and after treatment. Absorption after treatment was significantly reduced in both areas, demonstrating that the amount of calcite deposited via bioconsolidation is large enough to have a clear impact in absorption features.

Results of the peeling tests are also shown in Fig. 2. Since before and after tests must be performed in distinct zones, the graph presents average values obtained in each condition (untreated/treated). Averages were computed point by point following the sequence of measurements made in a same test spot; in total, 10 and 14 areas were tested, respectively, before and after treatment, to ensure result robustness. The peeling tests showed a significant cohesion increase after treatment, with mass losses 5-10 times lower than those before treatment.

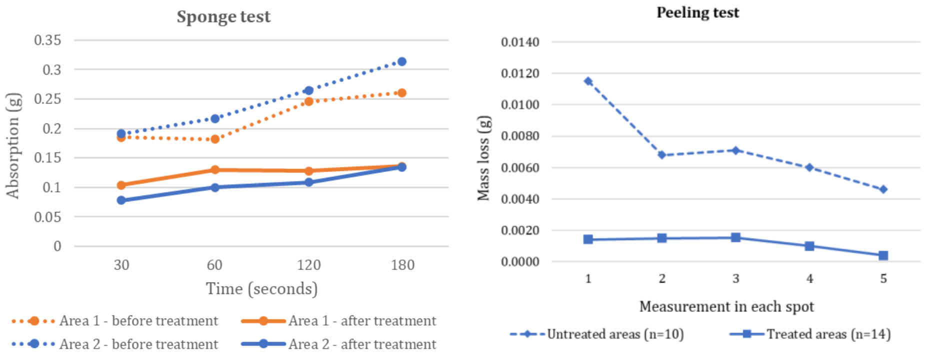

Fig. 2: Sponge test (left) and peeling test (right) results before and after treatment.

The Granada biomineralisation method, with Mixostone-M3P© as nutrient medium, has been proven effective and compatible in the lab (Rodriguez-Navarro *et al.* 2003) and onsite (Rodriguez-Navarro *et al.* 2015; Ettenauer *et al.* 2011; Delgado Rodrigues and Ferreira Pinto 2019). The tests in the Septimius Severus pilot corroborate these findings, indicating that consolidation was effectively achieved.

CONCLUSIONS

Gently touching the treated areas showed a clear improvement in the stability of the most deteriorated areas, and the tests demonstrated that the treatment was effective enough to induce some surface strengthening and reduce mass loss. On surfaces this valuable, consolidation must be carefully balanced to avoid excessive contrasts between treated areas and underlying substrates, to prevent long-term detrimental effects. The calcitic nature of both substrate and bioconsolidation product and the clear but low resistance increase confirm biomineralisation as a highly compatible process (Delgado Rodrigues and Grossi 2007), suitable for delicate and valuable surfaces as an upscaling treatment (Delgado Rodrigues and Ferreira Pinto 2019).

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

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Extended abstract

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 and sufficiently demonstrated options have been proposed, and the guiding principles on how to test, evaluate and decide on a stone consolidation treatment are still too short 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 supported 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 potential harmfulness is of much greater importance, although it is rarely considered as such. In fact, while the loss of effectiveness (translated as an insufficient cohesion increase) could in the end be compensated by the application of a new treatment, a problem caused by excessive harmfulness 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.

The evaluation of real cases is also not easy to carry out, as the harmfulness can take some time to manifest 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.

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 as a way to 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.

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. 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.

Conclusions and recommendations extracted from testing campaigns 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 try to reproduce the field conditions as far as possible, 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. 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.

In the full paper submitted to this symposium, 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.

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In situ consolidation of various monumental substrates in Crete (Greece): Application, evaluation and monitoring

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EXTENDED ABSTRACT

This work deals with the consolidation of various stones in 3 different case studies of monuments in Crete, Greece. The novel nanocomposite material was synthesized in the Lab of Materials for Cultural Heritage and Modern Building, incorporating into tetraethoxysilane (TEOS) nanoparticles of calcium oxalate (CaOx), which have been selected due to the compatibility to carbonaceous stones and the better resistance to weathering than calcite. Two emblematic Venetian monuments in Chania, Crete, Greece, the Bastian San Salvatore and the Arsenals in the old Harbour of Chania, both consisting of carbonaceous sandstones, have been treated with the nanocomposite (Figure 1). The decay of these stones was intense due to the sea salt influence and the strong northern winds that caused alveolization, pitting, rounding and mass loss of the construction materials. The 3rd case study was the Minoan palace of Kommos in South Heraklion consisting of limestones, suffered by alveolar disease, powdering and biodecay, as well as earthen-mortars that have been used as bedding and filling material in the rubble structures of the site (Figure 2).

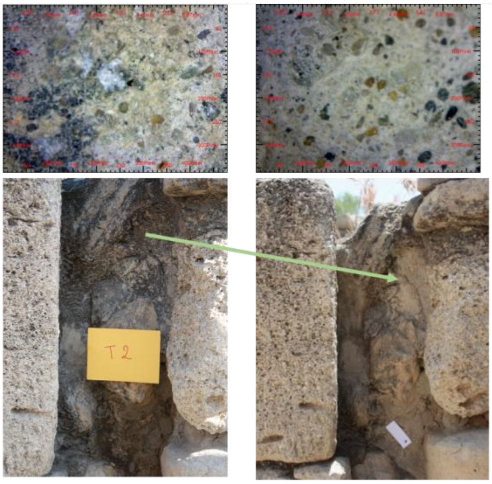
The areas with the intensive decay patterns were treated by brushing, spraying and through injection. The investigation of the different types of application showed that the brushing method was the most efficient for the monuments, since it has been more controllable without large consumption of the consolidant. The performance of the treatment was evaluated through measuring changes in various parameters, such as aesthetic alteration, water repellence, adhesion and mechanical properties. The techniques used for the monitoring of the consolidation were non-destructive, respecting the integrity and value of the constructions. In particular, color measurements, optical microscopy, peeling test, sponge test and rebound test were performed in situ without extracting samples and affecting the integrity of the monuments. Additionally, the above-mentioned tests were carried out in 1, 6 and 24 months after treatment, whereas a continuous monitoring is under progress.

The evaluation of the results showed that the consolidation achieved to adhering the decayed substrate, both stone and earthen-based mortars, whilst the water repellence was improved without altering the aesthetic parameters (Maravelaki et al., 2021a). Furthermore, the biological crusts were eliminated without their recurrence after at least 1 year. It could be argued that in all the case studies the consolidation was efficient, didn't alter the appearance of the monument and seems to prevent from further decay (Maravelaki et al., 2021b).

After treatment

Application of product

Fig.1_ Consolidation treatment with TEOS-CaOx.



Before treatment

After 6 months of treatment

Fig.2_ Application of TEOS-CaOx on earthen mortars, consolidation of the structure and removal of biodecay.

KEY-WORDS: Consolidation, Carbonaceous sandstones, TEOS with nano-calcium oxalate, water repellence, adhesion.

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Potential compatibility of alkoxysilane-based products to consolidate coarse-grained marble: The case of Trigaches marble

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KEY-WORDS: aged marble; alkoxysilanes; consolidation; incompatibility risks.

INTRODUCTION

Stones used in man-made constructions are considered durable materials, however, they are susceptible to various phenomena that cause their degradation (Delgado Rodrigues, 1989). Temperature variation has been pointed out as one of the major causes of granular disaggregation of marbles (Siegesmund et al. 2000), the so-called "sugaring", and loss of mechanical resistance, caused by the anisotropic thermal expansion of their constituent minerals (calcite or dolomite) (Steiger and Charola, 2011). Consolidation treatments have been used with the objective of re-establishing the cohesion of the degraded stone material. Fissured stones, like weathered marbles, can be easily penetrated by consolidants, thus some re-establishment of the cohesion is expected. However, consequences of the incompatibility of consolidation treatments are very difficult, or even impossible, to predict.

The undesirable effects that may arise from a poorly compatible consolidation treatment may lead to the total or partial loss of stone objects of high value, as they can accelerate degradation phenomena (Delgado Rodrigues and Grossi, 2007).

Considering the facts above, the present investigation aims to compare the potential compatibility of a set of alkoxysilane-based consolidants with a Portuguese historic marble variety having a coarse-grained texture. The approach was based on the methodology proposed by Delgado Rodrigues and Grossi (2007), which contemplates several criteria that are subdivide into a set of compatibility indicators rated according a scale of incompatibility risk from 0 to 10.

By integrating the ratings of the compatibility indicators into a mathematical equation, it is possible to obtain the final incompatibility degree (ID) of a given consolidation treatment. The ID of the tested treatments was computed as follows:

$$ID_n = \sqrt{\frac{C_1^2+C_2^2+\cdots+C_n^2}{n}}$$

where C_n are the ratings of each compatibility indicators and n is the number of compatibility indicators used for computing ID_n.

MATERIALS AND METHODS

Artificially aged Trigaches marble samples (40 x 40 x 30 mm) were treated with four alkoxysilane-based products by brushing until apparent saturation (assumed when the stone surface remains wet for 1 minute). The artificial aging was performed on dry samples by heating up to 300ºC for 1 h and then cool at room temperature according to the procedure described elsewhere, (Sena da Fonseca *et al.* 2021[1]). This procedure triggered internal stresses and the development of new fissures, Figure 1, that duplicated the porosity of the samples (1% after aging) and caused an ultrasonic pulse velocity reduction of around 50% in relation to sound samples.

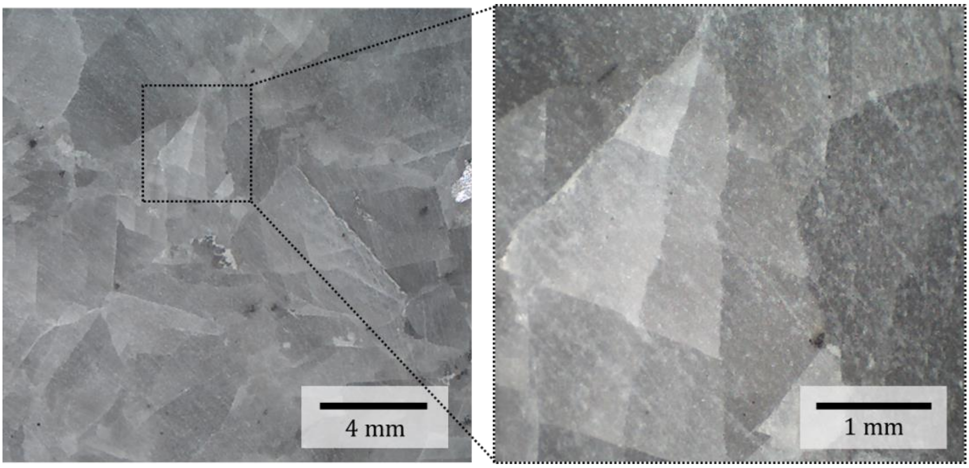

Figure 1. Trigaches marble after artificial aging.

The four alkoxysilane-based consolidants correspond to: a commercial product (Wacker SILRES® BS OH 100, hereafter BS-OH); a hybrid consolidant modified with polyethylene glycol (hereafter HCl.PEG) and two consolidants containing nanoparticles (hereafter HCl.nHAp and HCl.nSiO$_2$) (Sena da Fonseca *et al.* 2021[2]).

Samples treated with HCl.nHAp, HCl.nSiO$_2$ and HCl.PEG were retreated, one month after the first treatment, following the same treatment procedure.

The assessment of the potential risks of incompatibility of the consolidation treatments include diverse compatibility indicators such as the penetration ability of the consolidants within stone pores, and the alterations on the colour and water transport properties (water absorption by capillarity, water vapour permeability and drying) of the aged marble samples.

RESULTS AND DISCUSSION

All products revealed good penetration ability, which suggests that all consolidants have potential to increase somehow the in-depth cohesion of the aged samples. The treatments resulted from the absorption of around 2 kg/m^2 and left amounts of final consolidating materials comprised between 0.003 and 0.007 kg/m^2. The commercial consolidant was the one that left the highest amount of dry residue.

All treatments promoted total colour variations (ΔE^*) lower than 5, with BS-OH and HCl.PEG being responsible for the highest alterations, 4.8 and 4.0 respectively.

Water absorption by capillarity was the most affected compatibility indicator. All treatments promoted reductions around 60% on the coefficients of water absorption by capillarity (CWA), with exception of BS-OH. Although BS-OH caused a lower reduction of CWA (24%), it was responsible for the highest reduction in the total amount of absorbed water.

A reduction of water vapor permeability of the aged marble samples, between 20% and 40%, was promoted by the treatments. The highest and lowest reduction were caused, respectively, by the HCl.nHAp and HCl.nSiO_2 consolidants.

The drying behavior of the aged marble samples was not significantly affected by the treatments, with exception of HCl.PEG, that caused a significant reduction of the initial drying index (≈130%).

Taking all compatibility indicators considered in the assessment performed into account for computing the incompatibility degree (ID), the alkoxysilane-based treatments revealed ID values between 5,5 and 7,4 in a scale where 0 corresponds to a totally compatible treatment and 10 a totally incompatible treatment (Delgado Rodrigues and Grossi, 2007).

These ID values could be reduced if the multiplying factor predicted for fissured stones (0.6x) is applied, as suggested by Delgado Rodrigues and Grossi, 2007. In this case, the ID of the tested treatments is comprised between 3.3 and 4.4, with HCl.PEG and HCl.nHAp being the treatments with the highest ID of 4.4 and 3.8, respectively.

CONCLUSIONS

The different alkoxysilane-based consolidation treatments showed some risks of incompatibility when applied on an artificially aged marble with a coarse-grained texture, especially the HCl.nHAp and HCl.PEG treatments. This investigation gives new insights regarding the compatibility of alkoxysilane-based products with coarse-grained marbles in general and in particular with Trigaches marbles. The information obtained can be used to support decision processes for the selection of consolidant treatments and minimize the risks of negative consequences.

The present investigation can be further complemented with the inclusion of additional compatibility indicators, for e.g., thermal properties. The thermal behaviour of marble after being treated would be an important factor to be included in a future comprehensive analysis.

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

OBJECTIVES AND METHODOLOGY

The long-term interaction of sandstone built heritage with outdoor environments is recognized as a significant cause of decay. The combined action of chemical and physical mechanisms can progressively impair the integrity of the mineral matrixes. Crumbling, granular disintegration, and powdering 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 because of their chemical affinity to sandstone substrates, particularly in the case of eminently silicate mineralogy and their overall stability.

Several factors contribute to the final consolidation result, which ultimately arises from the complex interplay between the inherent substrate properties, the specific characteristics of the treatment material, the amount of applied product, the application methodology, and the curing regime. Ethyl silicate develops a consolidation effect thanks to its reactivity in the presence of water. Therefore, the curing conditions to which the substrates are subjected upon treatment are critical to the final strength development.

The present work investigates the impact of two different curing conditions on the consolidation of selected sandstones with a commercial ethyl silicate 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 ethyl silicate-based consolidant (Conservare OH, ProSoCo). 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 were monitored for up to 4 months of curing time.

A multi-analytical laboratory protocol was followed to characterize the distribution, penetration depth, and interaction between the consolidant and the sandstone substrates. The evolution of the silica gel was monitored by FTIR spectroscopy in ATR mode on microscopy glass slides to assess the rate and extent of the polymerization. Dynamic elastic moduli of the specimens before and after treatment were obtained by the ultrasonic pulse velocity method. The final increase of mechanical cohesion is a crucial factor for the evaluation of the consolidation treatment and was assessed integrating the results of laboratory testing of three-point flexural-tensile strength (Fig. 1) with a field-based method (drilling resistance measurements). Microstructural investigations were conducted on thin sections of reference and treated substrates via SEM-EDS analysis. Variations in the overall pore structure and water absorption behavior were investigated by mercury intrusion porosimetry measurements and standard water absorption tests by capillarity.

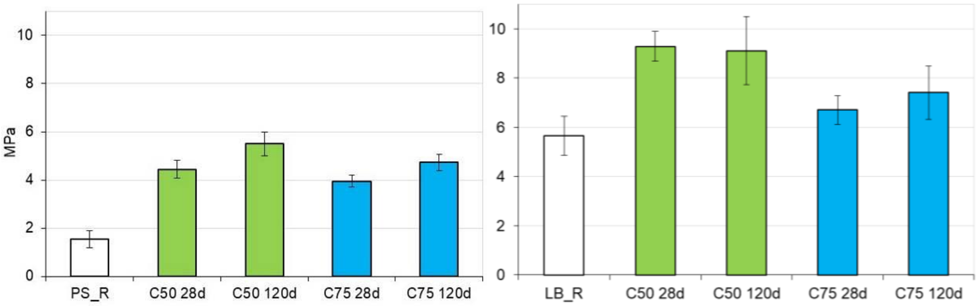

Figure 1 – Result of the flexural-tensile test (average values ± standard deviation, curing conditions and times are reported on the x-axis) of Prague (left) and Locharbriggs sandstone (right). Color codes: white, reference stone; green, after consolidation and curing at 50% RH (after 28 days and 120 days of curing); blue, after consolidation and curing at 75% RH (after 28 days and 120 days of curing).

CONCLUSIONS

The overall results confirmed that the curing regimes 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. However, the strength increase was much more limited when curing was conducted at RH higher than the reference one. The reduction of the consolidation efficacy was particularly relevant for Locharbriggs sandstone.

The microstructural investigation of the treated Locharbriggs also indicated a poor bonding of the silica gel, and the potential contribution of the clay minerals to such a result 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 porosity was observed after curing at high humidity. In such a condition, a significant alteration of the capillary water absorption behavior was also observed, particularly for the early-stage absorption rate of Locharbriggs, with possible implications for 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.

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

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

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 in outdoor and indoor environments, given its physical-chemical compatibility with stone substrates, and 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 most requiring a regular/even measuring surface. Moreover, these methods are able to measure relatively significant increments in surface resistance, but, except for the peeling test, 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 to try and ascertain their applicability to the field testing of surface hardness in stone materials of cultural value.

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, varying between 0 (full indentation) and 100 (no indentation) (Broitman 2017). 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.

MATERIALS AND METHODS

Two Shore durometers were tested for the assessment of surface hardness in a few Portuguese stone cube samples, typically found in heritage buildings, that frequently exhibit deterioration patterns related to their relatively high porosity / low resistance. The 5cm^3 samples (Table 1) included: Ançã (A) and Boiça (B) limestones, almost entirely composed of calcite; and two dolomite stones, one from Coimbra (D) and one from Lisbon (M). 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.

Table 1: Open porosity and compressive strength of the tested samples (fresh) (Ferreira Pinto and Delgado Rodrigues 2004); and surface morphology features.

Stone	**Open porosity (%)**	**Compressive strength (MPa)**	**Surface morphology** from *most regular* to *least regular*
Ançã (A)	27	36	Fresh Ançã > 2A90 ≥ 2A14
Boiça (B)	10	135	1B20 > 1B18
Coimbra (C)	18	89	1D66 > 1D68 ≥ 1D57
Lisbon (M)	15	143	2M4 > 2M2 > 2M33

Hardness measurements were obtained using two Shore durometers:

- a Sauter Professional Shore A HDA100-1 digital hardness tester (Balingen, Germany): standardised hardened steel indenting foot (35° cone); resolution 0,1/100;
- a Sauter Compact handheld Shore D HBD100-0 analogue hardness tester (Balingen, Germany) with drag indicator: standardised hardened steel indenting foot (30° 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 (Coimbra dolostone). The Shore A was used in all stone samples. The Shore D was used only in the Ançã and Coimbra stones, on dry specimens and after wetting the surfaces to try and mimic changes in surface hardness akin to those induced by subtle consolidation effects.

RESULTS AND DISCUSSION

With one exception (1D68 dolostone wet), all values obtained with the Shore A were above 80 HA, suggesting that the surfaces were too hard to be assessed with this device (Herrmann 2011). Standard deviations were relatively high, reaching 10.94 HA for the 2A14 Ançã limestone, and seemingly indicating that any measured small hardness increments, e.g. the distinction between the different dolostone samples, would probably fall within experimental error.

With the Shore D, the obtained hardness values did not surpass 85 HD; however, on average, value differences between wet and dry samples were generally very slight, particularly for the dolostone samples, and mostly fell within the standard deviation limits. The variability of the measurements was very high, and connected with the irregularity of the surfaces – dolostone samples, with the most irregular surfaces, had the higher standard deviations, reaching 13.44 HD for the 1D57 dry specimen.

The diagram in Figure 1 displays the average results, and respective standard deviations (error bars), obtained for the samples measured with both durometers.

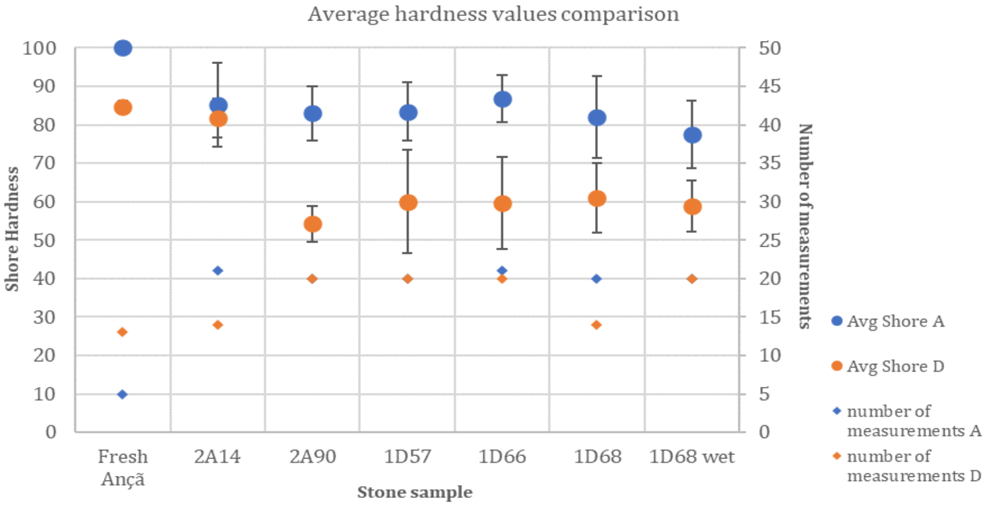

Figure 1: Comparison between average hardness values obtained with the two Shore durometers: Shore D seems to be less sensitive to small changes in surface hardness and more sensitive to rugged surface morphologies.

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. The Shore A, conversely, had overall comparable standard deviations for all stone types – fresh Ançã excluded –, varying between 6.10 HA and 10.94 HA, 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 Shore A durometer generally allowed less value dispersion than the Shore D durometer, arguably because the slightly sharper tip of the Shore D causes it to be more sensitive to surface morphology.

CONCLUSIONS

The onsite assessment of heritage objects is crucial not only for the correct planning and designing of conservation interventions, but also for their long-term monitoring, as well as to improve our knowledge on conservation solutions. However, when it comes to assessing the effects of consolidation actions, simple straightforward NDT field methods are scarce, and not necessarily able to capture the often times desirably subtle shifts in stone resistance imparted by the consolidant. The work presented here tried to ascertain the applicability of Shore durometers in 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 two 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. 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.

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Applied research on the consolidation of porous stones in Belgium

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KEY-WORDS: TEOS, DRMS, consolidation, porous stones, limestones

Extended abstract

Applied research on porous materials, such as products and methods to be used in conservation-restoration, is carried out in Belgium by an interdisciplinary team of the Monuments Lab in the Royal Institute for Cultural Heritage (KIK-IRPA, Brussels). The researchers of this lab have various educational backgrounds, including conservation, geology, chemistry, physics, civil- and industrial engineering. Every year, our lab receives numerous requests from regional agencies, communes, architects, contractors, and conservators-restorers to examine and propose optimal conservation advice for porous materials from masonry walls, murals, archaeological sites to (monumental) sculptures. Consolidation treatments are thus an essential part of the research as a solution to the problem of material loss caused by granular disintegration.

Products based on alkoxysilanes, specifically tetraethoxysilane (TEOS), are commonly used as stone consolidants, especially to treat siliceous stones. Other treatments are more effective for carbonate stones because of the limited affinity of alkoxysilanes with carbonate stones[i]. However, a wide range of TEOS-based products are available with significant differences in composition in terms of chemical structure of the active ingredient, catalyst, dilution degree, solvent, and additives. This variety of products produce different consolidating effects on different stone types. Additionally, the application methods, the amount of applied product and the environmental conditions, especially humidity, are crucial aspects to consider for the effect of these products. To assess the different effects of some TEOS-based products and methods on limestone, a survey by the Monuments Lab was carried out with a selection of commercially available products on the Belgian market. In contrary to what is claimed in literature, a significant consolidating effect on carbonate stone samples was observed. Based on this research and field experience, one specific product is now often considered in the framework of preliminary studies on the consolidation effect of weathered limestone. This TEOS-based product has been specifically developed for the consolidation of limestone with (according to the technical sheet) an active content of approx. 95(w/w)% to which a coupling agent to better adhere to a carbonate substrate is added (it can be assumed that the remaining 5% concerns the additive and not the solvent).

A relatively low dry matter content of 26(w/w)%, was measured at KIK-IRPA. This indicates that the molecules of the active ingredient are very small and volatile. The dry matter content is not only determined by the active ingredient, but also by its nature. In particular, the degree of polymerisation of the components (monomers and oligomers or prepolymers). After application, there is always a part of the product that evaporates and the more volatile the starting product, the lower the remaining content that can react to form silica gel. The lower the average degree of polymerisation of the starting product, the lower the dry matter percentage.

The need for consolidation is tested on each individual site before giving practical advice. Most of the requests for consolidation concern low weather-resistant types of porous sedimentary stones of Belgium's architectural heritage. Several stone types frequently occur, depending on the region and the historical availability. A small, but typical selection of natural stones are Lede stone (northwest Belgium) and the Brussels stone (centre Belgium), both relatively compact sandy limestones that are easily processed. The Maastricht stone (east Belgium and south Netherlands), a durable fine-grained, very porous, and extremely soft limestone is also used for research in stone conservation. A French limestone, Euville, also frequently occurs and is an interesting substrate for research since no successful consolidation treatments were possible, until recently. Euville stone is a coarse-grained crinoidal limestone with a porosity of 13 to 17% and widely used at the beginning of the 19th century for important monuments.

During the last decade, a standard research methodology has been developed to evaluate the need for consolidation and the practicability for each individual case. The initial step considers the determination of the stone type and the deterioration patterns, which are often carried out by visual observations, based on experience. When necessary, the on-site stone identification is confirmed by petrographic observation of thin-section. The procedure continues by conducting Drilling Resistance Measurements System (DRMS) conforming visually deterioration patterns. In certain cases, it is combined with the Scotch Tape Test, ultrasonic pulse velocity tests (indirect measurements), SEM-EDX observations.

The DRMS measurements on masonry elements are preceded by a selection of different locations based on the visual deterioration patterns and accessibility. These selected locations are representative of the whole masonry. One location consists of one or two stone blocks, and depending on the heterogeneity of the block, approximately five measurements points are executed. A consolidation treatment is considered based on the obtained hardness profile. If deemed necessary, a product and a method for the pilot treatment is selected based on the depth and degree of degradation. The standard test treatment method consists of two treatments. Each of these treatments consists of three separate applications of the product by spraying directly on the outer surface. The interval between the two treatments is 7 days and the total amount of product used is approximately 4 l/m^2. However, the product consumption varies greatly depending on the stone type and degree of weathering. Based on lab tests and experience, we consider that the number of treatments influences the degree of consolidation, while the number of applications effects the penetration depth of the product. DRMS drillings are repeated in the immediate vicinity of the initial drill holes one month after the last treatment because at this moment the temporary water repellent effect of the surface is mainly gone (this may take longer in our experience in case of dry conditions or if large quantities are applied). The mean results of the hardness profiles before and after TEOS-based treatment are compared. When a positive consolidation effect is achieved, the consolidation treatment will be recommended. When over-consolidation is observed, only one treatment will be recommended since this minimalizes the consolidation effect.

Three case studies following the consolidation of Euville stone are presented to show the successful consolidation of limestone with TEOS and the limitations of the methodology. Euville stone is a crinoidal limestone designated by geologists as a biosparite (according to Folk's classification) or as a grainstone (according to Dunham's classification). The limestone grains correspond mainly to crinoid ossicles (calcite monocrystals), cemented together by syntaxial sparite (well crystallised, clear calcite overgrowth around the limestone grains).

Some results of a research on a sculpture in Euville stone with granular disintegration are presented. According to the petrographic examination of two thin-sections, both intergranular microcracks and intragranular microcracks are common, with openings up to 100 µm. Two types of intergranular microcracks can be distinguished: cracks that follow the outline of the crinoid ossicles and cracks in the surrounding sparite cement. The latter are usually located in the centre of the sparite cement, at the suture between the syntaxial overgrowths. Intragranular microcracks occur to a lesser extent. The number of microcracks and degree of opening decrease with depth. SEM-EDX images give a good idea of the distribution of the silica gel in the microcracks in relation to the depth (Figure 1 and Figure 2).

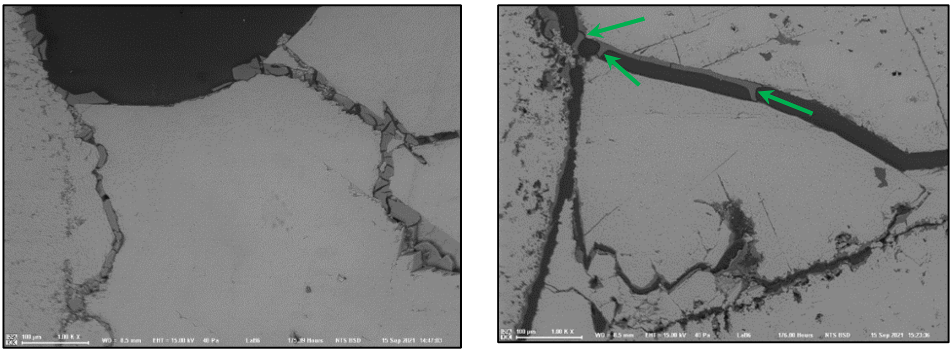

Figure 1 and 2. Back-scattered electron image of the surface of the stone (left) and at 5 mm depth in the stone (right). The limestone grains are medium grey, and the silica gel has a slightly darker tint. Point contacts of the silica gel are indicated by green arrows.

The silica gel is present in large quantities in the cracks and pores in the first millimetres and deeper in the stone still present but in a more limited quantity (figure 2). The well-known shrinkage cracks in the silica gel are observed, however the consolidation effect remains remarkably successful.

Figure 3 illustrates DRMS drill holes at the surface of a fracture area in the same Euville stone. Material loss can be seen around the hole which was drilled before the consolidation treatment (hole on the right), while a cohesive stone surface without granular disintegration is visible around the hole which was drilled after treatment (hole on the left). Figure 4 represents the mean values of the DRMS profiles obtained in the same area as in Figure 3 and indicates a granular disintegration before treatment (green curve) and an (over)consolidating effect after treatment (blue curve).

Figure 3: Detail of Euville stone with two DRMS drill holes (4.8 mm diameter). The hole before treatment (right) shows a significant material loss induced at the surface during the drilling, while the one after treatment (left) shows no material loss and coherent structure.

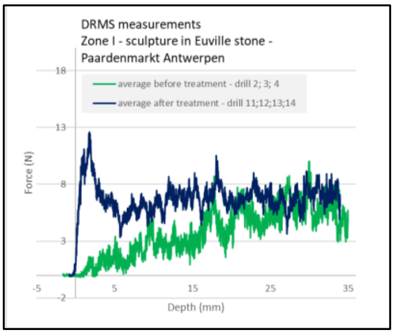

Figure 4: Mean values of DRMS measurements, before treatment (green curve) and after treatment (blue curve).

The results of the Scotch Tape Test in this case study confirm this increase in consolidation degree: the mean weight of the collected granulates performed after treatment contains 11(w/w)% of the mean weight of the collected granulates before consolidation treatment. More specific for the same zone in the fracture area as shown in Figures 3 and 4, the collected granulates after treatment represent only 0.77(w/w)% of the collected granulates before consolidation treatment.

These and other results of experimental tests in several case studies of Euville stone with granular disintegration show a significant consolidation effect after treatment with a commercial available product based on tetraethoxysilane. The long-term effect is not known and when it comes down to it, it is the most important factor in determining a good consolidation effect. This must be evaluated by monitoring it over time but given the generally limited access to the treated areas and the cost that this implies this is not always evident. These case studies are well-documented and the reports are digitally accessible which promotes adequate evaluations and research in the future.

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The phosphate-based solution used as carbonate stone conservation treatment: laboratory assessment of critical parameters and their influence on limestones

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INTRODUCTION

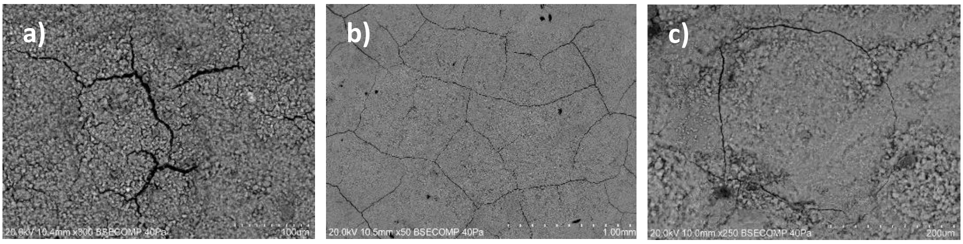
In recent decades, aqueous solutions of diammonium phosphate (DAP – ($(NH_4)_2HPO_4$)) have been used as a phosphate precursor to react with carbonate stone materials to form hydroxyapatite (HAP – $Ca_{10}(PO_4)_6(OH)_2$). Besides different compositions, this phase is considered more stable and insoluble than calcite (Ksp 25°C: calcite 4.8×10^{-9} mol/L, HAP 1.6×10^{-117} mol/L), with a potential role to play consolidating and protective effect or even to prevent bowing function on stone conservation (Sassoni 2018). However, it has been verified that the formation of HAP is not as immediate as initially expected and the formation of mixed calcium phosphate phases, with different molar ratios of Ca/P, has been detected. In addition to the difficulty in forming HAP, the characterisation of the different calcium phosphate (CaP) phases on carbonated substrates is also constrained by limitations in analytical techniques - for example, overlapping XRD peaks or vibrational bands in FTIR (Possenti et al. 2019). On the other hand, the effect of the aqueous DAP solution on carbonate materials dependents on several factors, with direct consequences on its performance, such as the pH and concentration of the phosphate solution, the application procedure, the contact time, drying and washing process of the treated surfaces, etc. Microcracking has been reported in the literature and verified in other tests performed within the scope of a larger study on the effect of phosphate-based solutions in Portuguese limestones (Cardoso, Costa, and Mirão 2016). This is an undesirable consequence when a consolidant or protective agent is required for stone conservation treatments. For these reasons, the influence of some relevant parameters in conservation practice, such as concentration and contact time of the DAP solution, on microcracking development was evaluated in two types of Portuguese limestones - oolitic and micritic limestone. Besides this aspect, surface morphology, colour change, characterization of the newly formed products - CaP, calcium and magnesium phosphates (CaMgP), DAP residues, other residues - and the CaP covering capacity of the treated surfaces were also considered on this ongoing research project.

MATERIALS AND METHODS

The diluted diammonium hydrogen phosphate solutions (0.3M and 0.6M) were applied by poultice, for 24h and 48h, on micritic and oolitic Portuguese limestones. The non-treated and treated specimens were observed at different scales. The characterisation of the new-formed products was analysed by Fourier Transform Infrared Spectrometer (FTIR). The micromorphology and elemental composition of the new CaP phases, the untreated and treated surfaces were observed by variable pressure scanning electron microscope with energy-dispersive X-ray spectroscopy (VP-SEM-EDS). The colour changes between untreated and treated specimens were determined using a portable spectrophotometer, using the CIELab colourimetric model to obtain the L*a*b* colour parameters and ΔE*(total colour change). The effect of the application of the phosphate-based solutions on the two limestone varieties was evaluated by water properties - water absorption by capillarity; mass variation was also used to evaluate the quantity of product inside pores after treatment.

RESULTS AND DISCUSSION

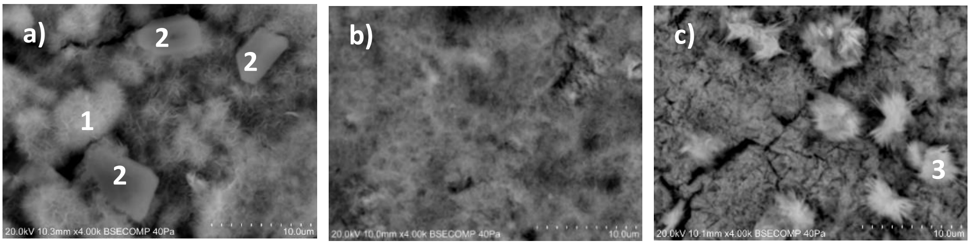
Compared to the non-treated surfaces, at the macroscopic observation level, there are no significant changes observed in the texture of the ML and OL treated surfaces. However, using SEM at different magnification, microcracking is observed in all test conditions of ML and OL. Some examples are presented in figure 1. Local (Figure 1a) and extended (Figure 1b) morphology/distribution? of microcracking can be detected on the ML treated surfaces. The thickness of the microcracks is around 1-3 μm. After contact with DAP solutions, all OL surfaces present higher roughness, with white, powdery aureole formation around the oolites, in particular for 0.6M-24h and 48h. The microcracks occur, preferentially, at the boundary between the oolite (calcite microcrystals) and the cement (calcite macrocrystals), with the formation of wide (≈10 μm), extensive and deep circular void zones (Figure 1c).



specimen ML-0.3M-48h specimen OL-0.6M-48h specimen OL-0.6M-48h (boundary oolite/cement)

Figure 1. Microcracks after treatment on ML and OL (different magnification).

Even without any quantification, a correlation between the concentration of the DAP solution and the occurrence of microcracking can be established: the higher the concentration of the DAP solution, the wider and more frequent microcracking becomes. However, contact time has no significant influence on microcracking development. The SEM observations show that the newly formed structures are fissured, i.e., micro-cracking may occur after the formation of the new compounds resulting from the reaction between the DAP solution and limestones. The contact of diluted DAP solutions (0.3M and 0.6M) with the ML and OL surfaces induced the formation of CaP and a very small amount of CaMgP after 24 or 48 hours. In the FT-IR analyses, the shoulder between 1080 and 1027 cm^{-1} (ν3 stretching mode of PO_4^{3-}) was detected in both ML and OL treated surfaces. This is indicative of the presence of the mixture of OCP and HAP phases. The presence of the bands 1641 cm^{-1} (H_2O bending), 559 cm^{-1} (ν4 HPO_4^{2-} bend) and 529 cm^{-1} (ν4 HPO_4^{2-} bend) indicate that OCP phases prevail. The Ca/P ≈ 1.3 also supports this finding. In both lithotypes, differences in the morphology of the new-formed products were found, which seem to be related to the morphology of the calcite crystals. Thus, they are identified: a) Needle-spherical individuals/aggregates, formed from each micritic calcite crystal (ML and OL oolites), which works as a nucleation spot to form CaP; Ca/P ratio ≈ 1.3, that can be OCP (Figure 2a-1); b) Homogeneous layer of nano-needles highly packed, with spongy/porous aspect or with a more compact structure; Ca/P ratio ≈ 1.399, that can be amorphous CaP and/or OCP (Figure 2b); c) Fluffy flakes, with lamellar structures and irregular shape, apparently isolated, emerging from the homogeneous layer of nano-needles highly packed; Ca/P ratio ≈ 1, that can be Brushite (Figure 2c). The CaMgP crystals are hexagonal, larger than the micritic calcite (Figure 1a-2).



sp. ML-0.6M-48h sp. OL-0.6M-48h-cement sp. OL-0.6M-24h-oolite

Figure 2. a) 1 - Needle-spherical individuals/aggregates; 2 – CaMgP crystals. b) Homogeneous layer of nano-needles highly packed; c) 3 - Fluffy flakes.

The experiments indicate that the reaction is incomplete, and residues of ammonium phosphates were also identified. Wide areas of calcite crystals are detectable suggesting that the reaction with DAP solutions is not uniform. In the first 24 hours, the reaction occurs more easily in the calcite microcrystals of ML and OL oolites; each microcrystal works as a Ca supplier and nucleation point for CaP formation. In the macrocrystals of OL cement, areas of calcite were observed, showing that the dissolution of calcite and reprecipitation of CaP did not occur as easily as observed in microcrystals. We can conclude that the texture and morphology of the crystals influence the occurrence of the reaction and the consequent formation of CaP. A similar result had already been observed by Naidu (Naidu and Scherer 2014). Comparing the 24h and 48h applications, the contact time with the DAP solution does not seem to favour the reaction between the DAP solution and the stone and the consequent CaP formation. It is worth saying that the marks of the cutting saw were also visible, which suggests that the layer of CaP should be very thin. After treatment, colour changes (expressed as ΔE) were observed in all specimens easily detectable by the human eye (ΔE >5). As expected, it was also verified a relationship between mass increase and the concentration of DAP solutions used. Relevant information is needed to clarify the distributions of new products formed inside the specimens, after treatment. A significant weight increase of the ML and OL specimens treated with DAP 0.6M was verified when compared to the more diluted solution (0.3M). That is, the more concentrated DAP solution promotes the formation of a large amount of new products, which can be reflected in the increase of specimen mass, in the reduction of water transport velocity and the water accommodation capacity inside the porous structure.

CONCLUSIONS

The contact of diluted DAP solutions (0.3M and 0.6M) with the ML and OL surfaces induced the formation of CaP and a very small amount of CaMgP after 24 or 48 hours. Mixtures of OCP/HAP were formed, prevailing OCP (hydrated phases such as Brushite and metastable amorphous phases) over HAP. The contact time of the solution does not seem to be determinant on the formation of microcracking. Instead, the increase of the DAP concentration promotes the microcracking formation on all treated stone surfaces, independently of the type of stone and contact time. The application of DAP solutions promoted colour alteration of the treated surfaces detectable by the human eye ($\Delta E \geq 5$). The decrease of water absorption by capillarity of the treated specimens were also verified. This indicates a decrease of the porosity, at least in the first millimetres of the surface after treatment. Ongoing research will clarify these effects and will allow us to evaluate other important properties, such as the characterisation of the mechanical properties of the treated surfaces.

Acknowledgements

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The European TC 346/WG3 standards on the evaluation of conservation works

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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.

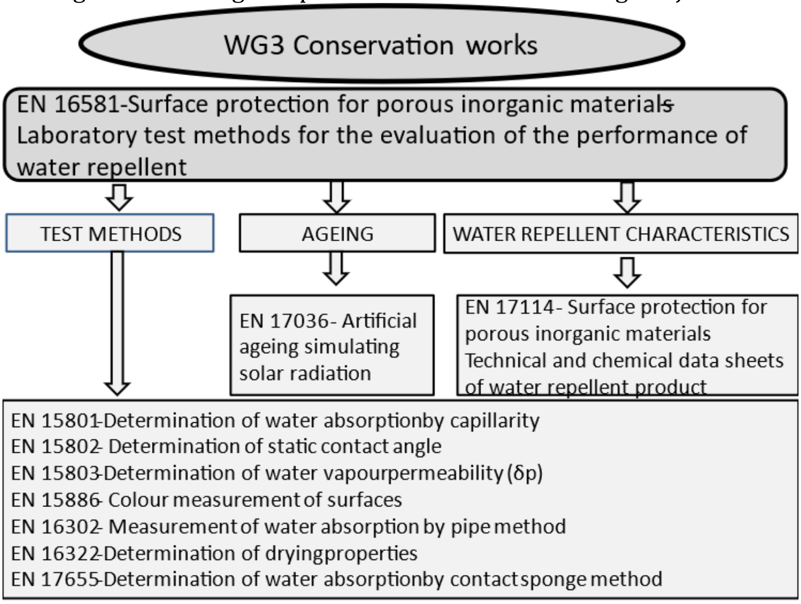

Fig. 1 Complete set of standards to evaluate the performance of water repellent.

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. According to the scientific community requirements to be achieved by a consolidant treatment are:

-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)

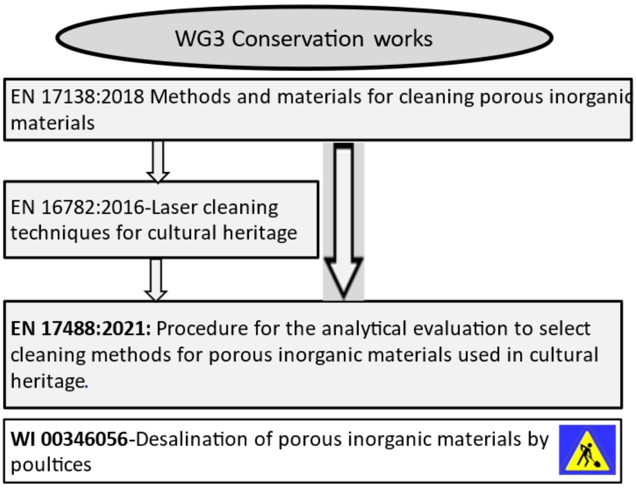

Figure 2. Complete set of standards to for evaluating and choosing products and methodology to be used for cleaning the heritage object surfaces.

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.

Peeling Test. The Scotch tape peeling test could be performed using an adhesive tape with known resistance to tensile load and adhesion capability (see ASTM D-3759 3330)

Portable 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.

Ultra-close range photogrammetry is based on the same principles of classical photogrammetry, but it is applied at a microscale.

Portable ultrasound equipment is a test rapid, non-invasive and economic.

X Ray Computed Tomography is a powerful non-destructive technique for the whole volume inspection of an object giving morphological & physical information.

μ-Computed Tomography can be applied by using conventional X-rays as well as synchrotron Radiation. The last one is a powerful technique e.g., in studying the effects induced by inorganic consolidant treatments on the stone microstructure.

KEY-WORDS: surface protection, cleaning, water repellent, consolidation treatments

From nanolime to nanobassanite: an improved approach for consolidation of stone and plaster

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SUMMARY: We report an improved solvothermal route for the production of portlandite ($Ca(OH)_2$) plate-like nanoparticles 50-110 nm in size with an unmatched high surface area of > 70 m^2/g, thereby ensuring a higher penetration into submicrometer-sized pores and enhanced carbonation rate when applied as nanolime dispersion in alcohol for stone consolidation. This route also serves as the basis for the production of bassanite (CaSO4·0.5H2O) nanorods, 120–200 nm in length, also showing the highest specific surface area reported so far and with enhanced reactivity towards hydration (forming gypsum). The latter can find direct application as "nanobassanite" alcohol dispersion for gypsum plaster consolidation.

KEY-WORDS: Nanolime, Nanobassanite, Synthesis, Stone, Plaster. Consolidation.

Different methods for the production of nanolimes and other alkaline-earth hydroxides have been developed in response to the challenge of counteracting the effects of the advanced deterioration of different elements of our cultural heritage affected by physical, chemical and biological alteration, whether natural or anthropogenic.

Over the last decades different conservation treatments, including consolidants and protective coatings, have been developed and applied to different heritage materials, stone in particular, in order to tackle this problematic issue. In a first approach to consolidation, synthetic polymer-based materials were applied, however, they were found to be highly incompatible with substrates such as stone, mortar and ceramic due to the decrease of breathability as a consequence of polymerization and surface film formation.

As an alternative, traditional consolidation treatments, more specifically limewater, were recovered. However, the relatively low solubility of calcium hydroxide in water makes it necessary to apply huge amounts of this product in order to produce a beneficial change in the mechanical properties of the substrate. In lieu of these limitations, one focus of research was placed on the synthesis of portlandite nanoparticles and their suspensions in non-water (alcohol) solvents, the so-called *"nanolimes"*, which have found extensive application as consolidants for stone and other building and decorative substrates. The most exploited methodologies for the obtention of *"nanolimes"* are the homogeneous precipitation of calcium hydroxide at moderate temperatures and/or in presence of organic additives, the controlled slaking of quicklime and the industrial controlled hydration of highly porous calcium oxide using steam. While these methods overcome the deficiencies of classic limewater, they still show weak points regarding production, and in some cases, performance. Most importantly, the presence of high amounts of water during synthesis and purification steps limits particle size selectivity and reactivity due to dissolution-precipitation coupled phenomena. An alternative to these synthesis processes is the heterogeneous solvothermal synthesis of nanolime particles in alcohol, using metallic Ca as alkaline-earth source. Yet, reported particle size (~150-200 nm) and surface area (≤ 40 m^2/g), seem to be a handicap to achieve optimal reactivity during carbonation and adecuate penetration into porous solids (Rodriguez-Navarro and Ruiz-Agudo, 2018).

Here, we report a novel and improved one-pot solvothermal methodology by which not only *"nanolimes"*, but also *"nanobassanite",* can be easily produced using calcium ethoxide as the main precursor following its controlled hydrolysis in the presence of organic solvents that catalyze this reaction yielding nanolime particles with size << 150 nm and surface area > 70 m^2/g. The latter results in enhanced carbonation and enable deeper penetration into submicrometer pores once applied as consolidants on stone. The same route can be modified to produce other nanoparticles that can be used for the conservation of a great variety of heritage materials. This is the case of "*nanobassanite*", which can be produced by the reaction of $Ca(OH)_2$ nanoparticles formed upon catalyzed hydrolysis of calcium ethoxide, followed by reaction with a sulfate source (e.g., sulfuric acid) according to the reaction (Burgos-Ruiz et al., 2021):

1. $Ca(OEt)_2 + 2\ H_2O \rightleftharpoons Ca(OH)_2 + 2\ EtOH$
2. $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4{\cdot}0.5H_2O + 1.5\ H_2O$

The importance of the development of this synthesis procedure lies in the obtention of cost-effective *"nanolimes"* showing particle sizes and reactivities without precedent. In addition, simple modifications of this methodology opens the doors for application on substrates other than carbonate stones or lime plasters and mortars, such as $CaSO_4{\cdot}0.5H_2O$ nanoparticles dispersed in alcohol for the consolidation of degraded gypsum plasterworks or alabaster sculptural works.

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Comparative study between ammonium phosphate and nanoconsolidants

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KEYWORDS: Hydroxyapatite; Calcium phosphates; Nanolime; Nanosilica; Marble

In the present study, a comparison was carried out between two commercial nanodispersions and ammonium phosphate as possible consolidants for a decayed byzantine marble sarcophagus in Ravenna, Italy. Nanolimes and nanosilica were taken into consideration as they have been receiving increasing attention in the scientific literature and in the onsite practice, thanks to their advantages compared to traditional consolidants, such as limewater and ethyl silicate (Giorgi et al., 2000; Rodriguez-Navarro and Ruiz-Agudo, 2018; Pozo-Antonio et al., 2019). Ammonium phosphate was also considered, as it has shown very encouraging results for both consolidation and protection of carbonate substrates, such as marble, limestone, lime-based mortars and renders (Sassoni, 2018). The three consolidants were tested both in laboratory conditions and in the field. In the laboratory, artificially and naturally weathered marble specimens were treated by the three consolidants applied by brushing and, in the case of ammonium phosphate, also by poulticing. After curing, the treatment effects were compared in terms of composition and morphology of the new phases, penetration depth, increases in cohesion, color change, alterations in the pore system and water absorption. In the laboratory, the ammonium phosphate treatment proved to be more effective than commercial nanoconsolidants, which exhibited low penetration depth and, in the case of nanosilica, lack of chemical bonding to the substrate, as expected. The ammonium phosphate treatment exhibited higher penetration depth and higher consolidating effectiveness, especially when applied by poulticing. In terms of aesthetic appearance, alterations in open porosity and water transport properties, all the treatments proved to be fairly compatible. When tested in small areas of the marble sarcophagus, all the treatments showed lower consolidating capacity than assessed in the laboratory. This was due to the fact that the part of the sarcophagus subjected to field testing (which was selected as it was the least visible part) was actually in quite a good conservation state. Putting together laboratory and field results, ammonium phosphate applied by poulticing was regarded as the most promising treatment, which was hence applied onto the whole sarcophagus. After consolidation, significant increases in marble cohesion were registered by ultrasounds, especially in the most deteriorated parts of the sarcophagus, where thermal weathering had caused significant grain detachment and loss. In terms of aesthetic compatibility, no significant alteration of the marble appearance was detected by

naked eye. The results of the present study point out the high potential of the ammonium phosphate treatment, not only in laboratory conditions but also in a real case study. In addition to its higher effectiveness and good compatibility, ammonium phosphate has also the advantage of being effective after just 24 hours, whereas nanosilica requires curing for a few days and nanolimes for at least one month. The results of the present study are expected to contribute to the further diffusion of the ammonium phosphate treatment in the practice of stone consolidation.

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Identification and characterization of the decay patterns of stone reliefs from the Tāq-e Bostān historical site of Iran

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INTRODUCTION

Tāq-e Bostān historical site related to Sassanid Empire of Persia (224-651 CE) that is a stone complex which was carved from the bedrock of Bistoon-Parao Mass of Zagros Mountain, at northern of Kermanshah city, western Iran. Bistoon-Parao Mass is mainly composed of calcareous stone (Mohammadi et al. 2018). This historical site includes two barrel-vaulted halls, so-called “Great Arch” and “Small Arch”, and an open relief panel called “Ardeshir II” (fig. 1).

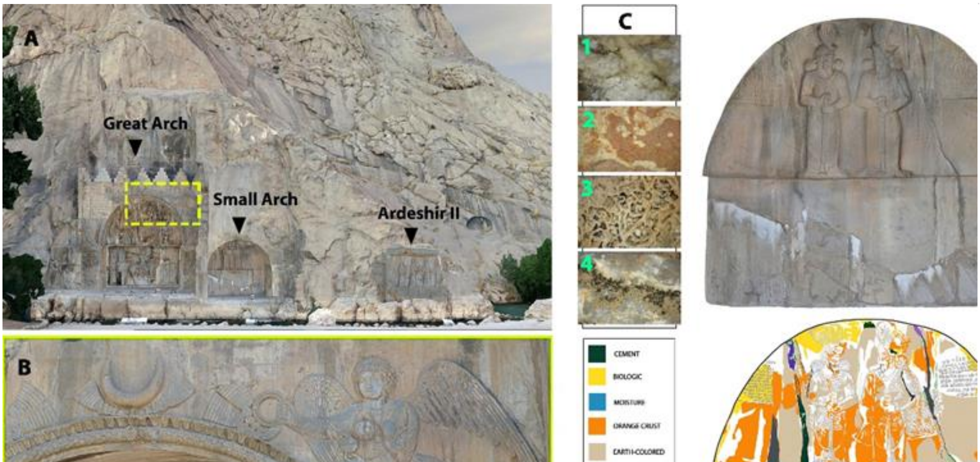

Figure 1 A. Tāq-e Bostān historical site; B. detail of the yellow rectangle in (A) that shows contamination and crusts; C. macroscopic details of (1) black crust, (2) patina crust, (3) biologic by-product; (4) black spots of the unactive micro colony of fungi; D. integrated white efflorescence at the bottom of the Small Arch; E. a sample of the categories map of damage from the Small Arch.

The Great Arch (8.9 m in height, 7.8 m in width and 7 m in depth) and the Small Arch (5.3 m in height, 5.8 m in width and 3.6 m depth) are cut back into the rock. This stone complex has endured almost 17 centuries exposing to weathering. Tāq-e Bostān includes carving reliefs of Ardashir II and Shapour III (the Sassanid's kings) (Fukai et al, 1984) as well as the finest stone sculpture from the Sassanid period. The relief patterns accentuate power, glory, honor and religious tendencies from the Sassanid period, but nowadays, they have been covered and deteriorated the surface of the reliefs (mostly in the Great Arch) in orange to brown and even black colors, so that the subtleties of Sassanid motifs have remained hidden from public view. Some evidence of efflorescences in white color and freezing phenomenon (superficial detachments) are visible. Given the importance of the reliefs and exposure to weathering phenomena which may cause severe damage to the fine relief patterns due to consecutive deterioration of the stone, it is essential to conduct field survey and identify decay patterns. Therefore, the aims of this study are the identification and documentation of the decay patterns and characterization of their chemical composition.

METHODS

In the field, the decay patterns of stone reliefs were investigated by field studies and macroscopic investigation (Dino-Lite Edge AM4115ZT). Documentation of the decay patterns was registered by photography (Nikon D810 Full-frame) in 1:1 and then the map of damage categories was prepared by CAD software. To characterize the chemical composition of deposits (Black to white crusts), an analytical study was performed by using X-ray diffraction (XRD). XRD analysis was undertaken using D8ADVANCE model (Bruker Company, Germany) with the analysis condition of CuKα (λ =1.54 Å).

RESULTS AND DESCUSSION

The decay patterns of Tāq-e Bostān have been categorized in 6 main groups (fig. 2).

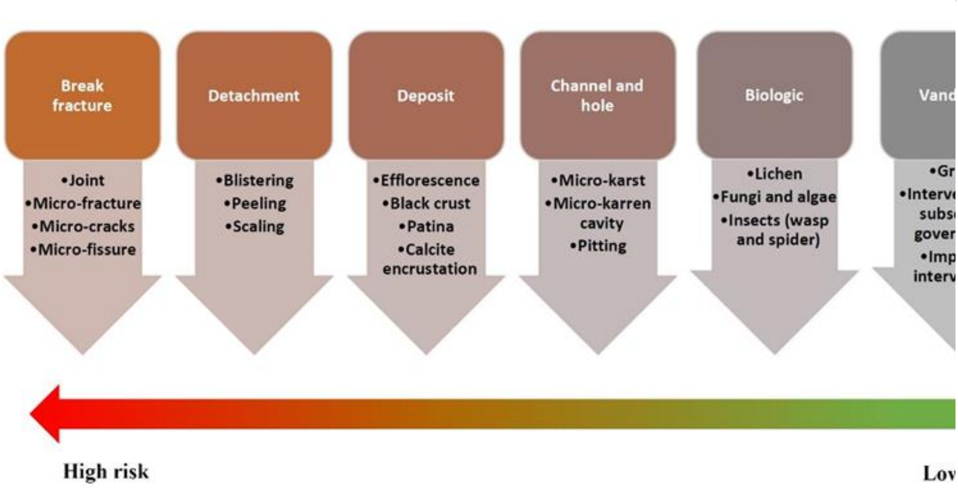

Figure 2 Decay patterns of the Tāq-e Bostān historical site arranging relative to their risk assessment

Graffiti, which is one of the widespread damages, was obtained through scratching among the reliefs. Some evidence of bio-pitting was observed by the macroscopic investigation that happened during more than a millennium. Pitting pattern due to lichen activity in this area has caused distortion and roughness of the surface. Now, there is no lichen activity; this is promising because periodical cleaning has prevented lichens growing again. Field studies showed that the colorful crusts have distorted most of the reliefs (especially the Great Arch). The crusts of the Great Arch originated mainly by the water ingress from the natural channels inside the rock that has spread the deposits among the reliefs. Also, the restoration interventions such as cement used to fill the joints and fractures have caused the formation of salt efflorescences and microcracks in the surrounding areas. XRD analysis of scattered efflorescence identified two major phases of calcite and gypsum and minor of weddellite and quartz. This indicated the scattered efflorescence are sulfate salt extended over time by water percolation and drainage in which probably the source is sulfate-rich cement used in restoration. XRD Analysis of the earth-colored layer shows that the main component of this deposit are calcite (substrate), quartz and montmorillonite ($Al_2O_3.4SiO_2.xH_2O$) as a minor phase. Montmorillonite is an unstable, acid-soluble clay that can be removed with distilled water (Ramos et al. 2014). This type of clay is very soft, which can be deposited from water solutions. XRD results of brown crust indicate that this crust, like the earth-colored layer, consists of a significant amount of a major component of calcite phase and, montmorillonite and then quartz as the minor phases. Thus, the brown color is related to the accumulation of unstable clay minerals of the acid-soluble montmorillonite. Result of XRD analysis from black crust shows calcite and gypsum as major phases and quartz as a minor phase. Since the stone of the Tāq-e Bostān is almost a pure limestone and the air pollution of the area is under control (Shekofteh 2019), the source of gypsum of the black crust is probably sulfate-rich cement that was used for restoration. Therefore, SO_4^{-2} dissolved in water (outflow water from the natural channels on the cement area) with Ca^{2+} which is released by dissolution processes from the calcite of bedrock (Pozo-Antonio et al. 2021) form the gypsum black crust. XRD analysis of the orange patina reveals the calcite phase as the major amount. Quartz and gypsum phases are approximately the same and the minor phase is calcium oxalate (weddellite $CaC_2O_4.2H_2O$) The oxalate phase is minor because it is a very thin layer (around 80-150 μm in average) and just covers the surface of the rock (Doherty et al. 2007). Oxalate is nearly always adjacent to the black crust (Gadd et al. 2014), that is the reason for the presence of gypsum phase in this sample. The presence of weddellite is promising because calcium oxalate patina is very stable and it can protect the surface of stone against further weathering (Chen, et al. 2000). XRD analysis of integrated white efflorescence from the Small Arch identifies two major phases of calcite and portlandite (major) along with the quartz phase as minor. It is interesting to identify the calcite phase, in particular portlandite, as the major phase of this type of efflorescence that indicates calcite encrustation. This phenomenon and the presence of portlandite show the process of calcite encrustation is still active. Thus it became clear that water ingress among the reliefs caused dissolution and formation of crusts on the surface of the stone which can be controlled by directing the water away from the reliefs. The high risk part of deterioration patterns is the natural joint (break fracture) of bedrock that is stable at this moment but it is not under control in the case of movement.

CONCLUSION

From the point of decay patterns, the reason of formation the black crust and white efflorescence is water egress through the micro-karst (micro-karren cavities) inside the ceiling and walls, which is the result of stone dissolution and carrying soil and sulfate elements within. In fact, the main decay factor in Tāq-e Bostān historical site is water dissolution. Hence, water flowing along with the activity of microorganisms and previous incorrect interventions, are the most important factors of deterioration that destroyed the surfaces of reliefs of the Tāq-e Bostān which should be under control.

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Consolidation of the glaze-ceramic body Azulejo interface

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KEY-WORDS: Azulejo, glaze detachment, deterioration, consolidation

INTERFACE DETERIORATION AND GLAZE DETACHMENT

The azulejos are one of the most important art forms in the cultural heritage of Portugal. They are composite materials constituted of a ceramic body and a glaze layer where the painting that bears its artistic value is usually incorporated. In the last decades, a general accelerated decay of architectural glazed ceramics has been observed, namely in Portuguese azulejos, resulting in the irreversible loss of the totality or parts of the glaze layer and therefore the loss of their artistic value.

The interface between the glaze and ceramic body plays an important role in the tile's degradation mechanism (Mimoso and Esteves 2016). The different properties of the glaze and ceramic body induce differential behaviour in terms of the hydric and thermal expansion, especially when subject to stress conditions such as temperature cycles, presence of salts and humidity in the supporting walls. Water from the exterior may also come into action by penetrating through unglazed or fissured areas and will add to the development of large stress on this interface inducing crazing, delamination, and ultimately detachment of the glaze layer.

The decay of the glaze-ceramic body interface is known to be usually initiated at discontinuity areas such as edges of the tiles, edges of glazed-unglazed areas, glaze pores, or glaze crack fissures. However, the fissures of the glaze layer (cracks) are usually considered part of the identity of the tile and not an issue to be tackled in their conservation. The crack fissures constitute nonetheless a direct connection between the biscuit and the environment, giving rise to moisture exchange, concentration of contaminants, salts crystallization, and providing biologic agents a protected locus for growth therefore promoting the tiles degradation. Two types of cracks are usually observed, which we call “Type I” and “Type II”, where type I are those that propagate directly into the biscuit while type II propagate through the glaze-ceramic interface (Figure 1) (Mimoso, Pereira, and Silva 2011; Mimoso and Esteves 2016). Type I craze can however develop into Type II, anticipating the glaze detachment (Mimoso and Esteves 2016; Mimoso, Pereira, and Silva 2011).

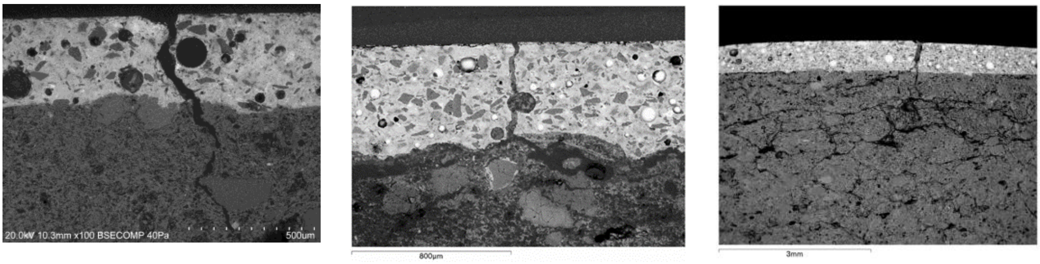

Figure 1. SEM observations of crazed tiles in risk. Type I crazing (left); Type II crazing (middle); and highly advanced ceramic body deterioration presenting type I and Type II glaze crazing (right).

COMMON CONSOLIDATION TREATMENTS

Despite the importance of preventing or halting the glaze detachment, no conservation treatments specifically aimed at the consolidation of the undetached glaze-ceramic interface area have been proposed so far. Mass consolidation is the conservation method generally applied to improve the ceramic body cohesion and simultaneously try to promote the glaze-ceramic interface adherence. For a mass and more in-depth consolidation (necessary if aiming to reach the non-accessible glaze-ceramic body interface) immersion of the entire tile in a consolidant solution is the method usually used. When the glaze is lifting and there is direct access to the interface (or when the glaze is already detached) a local consolidation of the detached ceramic body area can be performed by brush or syringe. The most common material applied for consolidation is the acrylic resin Paraloid B72® on a low concentration in acetone or xylene, however acid silicate esters (such as TEOS – tetraorthosilicate) are also being applied (Mendes et al. 2015; Pereira et al. 2012).

Mass consolidation of the tiles is the only method usually applied to reach the interface of the glaze- ceramic body. However, this method has shown several limitations regarding its actual consolidation effect, namely at the interface level. If during the consolidant polymerization stage actions are not taken to slow down its evaporation rate (Buys and Oakley 1993), the resin migrates back as the solvent evaporates (Costa et al. 2015; 2017), resulting in the drying and polymerization of the consolidant mostly onto the unglazed ceramic surface. Besides the insufficient consolidation at the glaze-interface level, this accumulation at the back of the tile further impairs the adherence to the support (Santos 2013). The hydrophobic character of some of the consolidant agents together with the resulting decreased porosity of the consolidation can difficult the rea-application of the treated tiles on the architectural support. Another drawback of the mass consolidation method is the necessity of having the tiles removed from the wall, which does not allow their *in-situ* consolidation.

CONSOLIDATION VIA THE GLAZE LAYER

With this work a novel method of consolidation through the cracked glaze surface of the tiles is presented. This new technique has the advantage of allowing for *in-situ* treatment of the tiles and the specific consolidation of the glaze-ceramic interface area. By allowing the consolidant solution to penetrate via the glaze fissures, the area close to the crack is imbibed first, slowly advancing to the underlying glaze interface and core of the tile (Figure 2). Under this concept, it is expected to have the recession of consolidation solution towards the small evaporation areas provided by glaze fissures leading to the consolidant polymerization close to the crack areas, increasing the cohesion of the ceramic and in principle the adherence of this highly precarious area. The polymerization at and close to the glaze fissures can also lead to the obstruction of the fissure's connection with the environment and to some extent reduce the discontinuity of the glaze layer. Because of the local consolidation action, if timed properly, the consolidation solution may also not reach the back surface of the tile, avoiding or minimizing the loss of adherence to the wall support mortar, as happens when mass consolidation is executed.

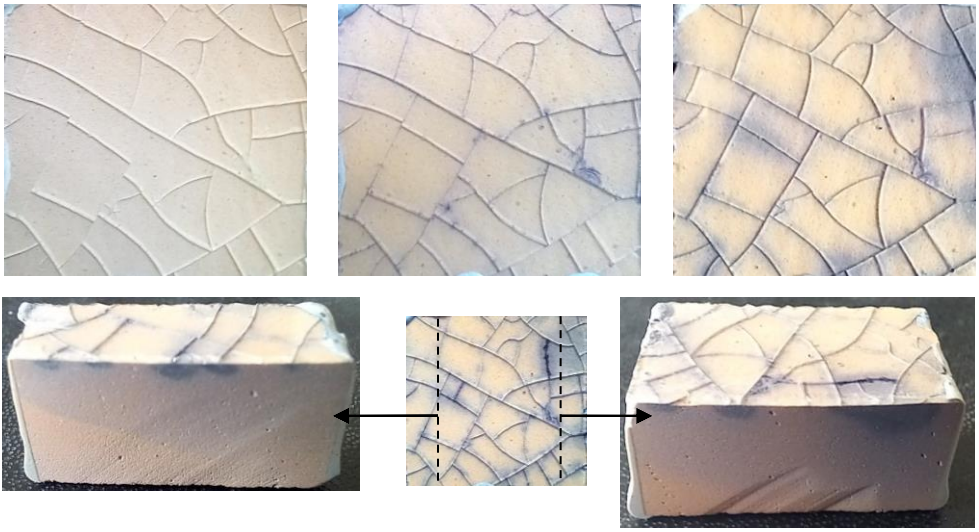

Figure 2. Visualization of the imbibition profiles in time using a dye solution as medium. Tile cross-sections showing the absorption/evaporation front that does not reach the back of the tile and the accumulation of the dye in the areas close to the crack fissures.

In this work this novel method of local consolidation of the crazed glazed tiles is therefore presented and their potential advantages and limitations discussed. Different consolidant solutions are presently being tested together with the in-situ consolidation methodologies to study the efficacy of the proposed treatment.

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The assessment of the consolidation action with DRMS: an overview

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KEY-WORDS: drilling resistance, penetration depth, DRMS

INTRODUCTION

Stone decay can be expressed by several types of alteration forms with direct impact in the erosion of the surfaces, namely, *disintegration* (detachment of single grains or aggregates of grains) and *scaling* (*flaking and contour scaling*) (ICOMOS, 2008).

Disintegration can affect only the surface but usually it affects the stone in depth. Damage starts from the surface, can reach several centimetres in depth and depending of the type of material can lead to powdering or sanding. Very often *profiles* with strength increasing towards the interior can be identified, which can be accompanied by differences of porosity and other relevant properties.

Much has been researched and written since the seventies of the last century when consolidation products were presented as solutions for mass consolidation of decayed materials, especially limestones, sandstones and marbles, the most frequent materials used in the built heritage.

The search to establish methods capable of evaluating the *effectiveness* of treatments or the *potential harmful effect* that is generally inherent to them is still an ongoing process. From the author's point of view, one of the most conceptually structured proposals for the evaluation of conservation treatments (including those with consolidating action) was presented in Dahlem Workshop in 1996 (Sasse and Snethlage, 1997). If it may be considered too exhaustive and complex procedure, it can be adapted for the selection of the most relevant aspects according to each specific case. At that time, some questions were raised: ”can *we predict a better effectiveness and durability of one treatment against another on the basis of these measurements and requirements*?” but at the end it was considered “*that is evident that a technology of stone conservation is still missing”.* Quite surprisingly they could have been made today despite the technological advances of recent years in the field of Conservation.

“*Homogenous strength profile, strength increase up to strength of unweathered stone*” is indicated to be evaluated with *“drilling hardness”* applicable on the objects.

“*Penetration depth*” of the treatment is very relevant not only for the evaluation of efficacy but it can also inform about the potential harmfulness and stability of the treatment over time.

GENERAL ASPECTS OF THE METHOD

DRMS (Drilling Resistance Measurement System) is a method that uses microdrilling technique for the characterization of the consolidation action of treatments applied on stone materials, both in laboratory and field conditions (Tiano et al. 2000).

The method is micro destructive: it makes a hole of about 5 mm in diameter and measures the drilling force needed to make this hole under controlled rotation speed and penetration rate. It is particularly useful for low and medium hardness stones, homogeneous materials and it is very useful to make in-depth resistance measurements.

The presence of quartz grains introduces great variations and require specific testing and interpretation strategies. The experience had shown that it is possible to tackle the "*heterogeneity* of the materials" and the effect of *abrasivity* of drill bit that introduce an artificial effect on the results. Besides the modification of the protocol of testing, it may require the correction of raw data (e.g. for the "abrasivity effect") (Delgado Rodrigues, Costa, 2004).

For comparison purposes the conditions of tests (rotation speed and penetration rate) must be kept unchanged. The correlation with other conventional mechanical properties (compressive or flexural strength) is considered very relevant but up to now only a few of such exercise were done.

Granites, even very decayed, are out of the range of the load cell and the method is not applicable to them.

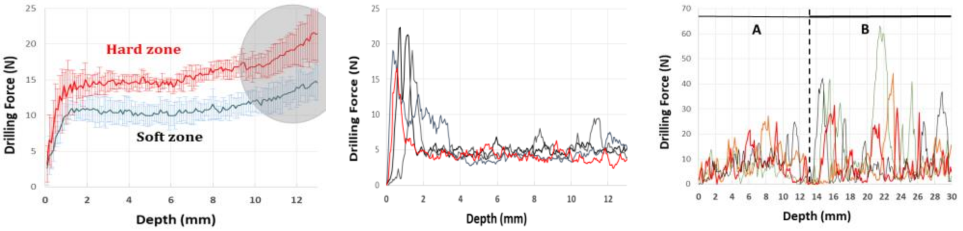
IN SITU PROFILES: SOME EXAMPLES

In this presentation the objective is to emphasize the relevance of the information that can be registered in situ when the characteristics of the decayed surfaces to be treated are particularly relevant.

Weathering/decay stone profiles

Drilling tests performed on a decayed surface (Figure1.a) unveils a "continuous strength" profile until about 8-10mm, but discriminate zones with different harnesses ("soft" and "hard"). The first couple of millimetres of the curve are largely influenced by the shape of drill bit. If a planar drill bit can be used, the decay profile can be more clearly identified. In some cases, the "packing effect" due to sand accumulation is perceived as an artificial increase of the values, which makes the characterization at that depth impossible (grey circle, Figure 1.a). On the contrary of what could be expected, the presence of some moisture can also contribute to this effect. In fact, the presence of moisture reduces the mechanical strength and measurements are supposed to be sensitive to the environmental conditions prevailing during the tests. Besides the type of dust produced, the experience had shown that some test conditions (rotation speed/penetration) may enhance this negative effect.

The presence of hard and irregular superficial "layer" of about 4 mm was identified in a different but also very soft limestone (more heterogeneous than the previous one) (Figure 1.b). The origin and the composition is unknown and was not investigated. Profiles on mortars are very different (Figure 1.c). The presence of large force peaks are typical of mortars due to the presence of quartz grains in a softer binding matrix. The profiles are more difficult to interpret. However, even in raw data format, they can be informative and identify the application in “two layers design”. Two zones are present: the external layer A (10-15 mm) is softer than the internal one (B).



(*300 rpm,20mm/min*)
a) soft and homogeneous limestone

(*400 rpm,15mm/min*)
b) soft limestone, with quartz grains

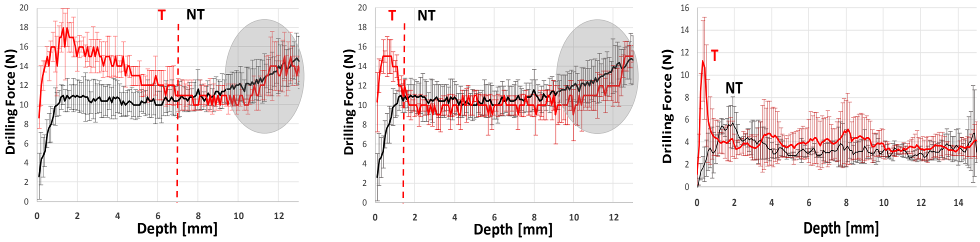
(*100 rpm,10mm/min*)
c) lime mortar (Costa et al. 2012)

Figure 1. Profiles on surfaces made on soft stone and similar materials using DRMS

Profiles of treated limestone surfaces

The use of consolidants recognized by the ease of penetration capability, such as the conventional ethyl silicate family products, are easy to identify, particularly when applied to homogeneous or moderately homogeneous rocks (Figure2a). The treatment profile obtained with an acrylic resin (here exemplified by Paraloid B72) is different and, in this case, mainly due to the migration capability of the product, which is reflected in the hardness of the stone treated fringe (Figure 2b). The graphs obtained show the differences recorded when both products where applied by brush, in conditions considered to be comparable. Contrary to what very often happens, differences are mainly due to the *penetration depth* and in the smooth or abrupt changes of the hardness of the treated area until the front is reached.

Inorganic treatments are usually much difficult to detect except when they promote a rigid layer at the surface (Figure 2c). Very small effects on consolidation action combined with heterogeneous substrates are a challenge not always possible to overcome.



(*300 rpm,20mm/min*)
a) soft and homogeneous limestone treated with *an ethly silicate*

(*300 rpm,20mm/min*)
b) soft and homogeneous limestone treated with *Paraloid B72®*

(*400 rpm,15mm/min*)
c) soft limestone, with quartz grains treated with *inorganic consolidant*

Figure 2. Examples of profiles of stone consolidation treatments applied on pilot zones

Inorganic treatments are usually much difficult to detect except when they promote a rigid layer at the surface (Figure 2c). Very small effects on consolidation action combined with heterogeneous substrates are a challenge not always possible to overcome.

Besides efficacy, the use of the information provided by the comparison of the profiles before and after treatment is also very relevant for the evaluation of the nocivity of the consolidation treatment. Rigid layers at the surface are clearly a risk of future detachment and the development of application protocols should also take this information into consideration.

FINAL REMARKS

As it is well recognized, the assessment of consolidation treatments should combine laboratory and *in situ* assessment validation. Samples used in laboratory studies rarely represent the surfaces to be treated. Protocols and application methods are crucial for the final result obtained after treatment and frequently they also differ in the two approaches.

Despite being micro-destructive, sometimes requiring some expertise on the interpretation of data, DRMS is a sensitive technique that provides very useful information about real object surfaces and the consolidant effect applied on it. The interpretation of data can also be improved if other methods can be used to complement the information.

The value of its use in the laboratory is more recognized. The vast number of studies that use it clearly indicate it. We can say that it constitutes a tool that yet has no parallel for the purpose of measuring how the cohesion and lost resistance are recovered after treatment.

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Presence of salts requires inclusion of kinetic issues when consolidating objects

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KEY-WORDS: salts, salt mixtures, kinetics, wall paintings, consolidation

UNSOLVED RESTAURATION CASES

Salt-contaminated vaults will require, to some extent, minor or major, consolidation of the surfaces. One among many examples of salt contaminated vaults requiring consolidation is the one in Rørby Church, Denmark, which has one of the most valuable wall paintings from the Gothic medieval age in all Scandinavia. Back in 1981-82, some of the vaults were uncovered, leaving one vault untouched due to presence of salts in the masonry. A second case, is the Vä church in Scania, Sweden, with extraordinary Roman wall paintings from the early 12th century. Here the former conservation campaign was put on hold due to a lack of a thorough examination of salt presence and climatic conditions. A third case is Vrigsted Church, Denmark. Here the advisory authority decided to uncover the wall paintings in the whole interior of the church and leave the heavily deteriorated surfaces as found without thorougly analyzing the salt content in the construction materials and plaster layers. Neither was the long term effect of heating combined with moisture and salts studied thus allowing possible damage evolution.

PLASTER LAYERING CHALLENGE: CONSOLIDATION CHOICE

When addressing original deteriorated materials, the objective is to strengthen these materials or reconstruct them. In general, an increase of the material density might be apparently sufficient, but in others a reconstruction might be needed. When soluble salts are present, some of the salt ions may reach the surface during evaporation and result in harmless salt efflorescences; this depends on the specific material properties (Laue et al. 1996), and the areas near the surface are of special relevance. The complexity of layered structures is well-known in relation to wall paintings, which typically consists of multiple layers of render and grounds, as shown in figure 1. Here face breaks in the capillary pore structure may occur intermittently and on a small scale. These breaks in pore structure may result in an accumulation of salts at the various interfaces as the water evaporates out of the system, leaving the salts to crystallize. Obviously, this exacerbates the situation and can be expected to lead to enhanced deterioration (Cather 2003).

This phenomenon was preliminary studied visually on an unpolished cross section from the covering layer of a wall painting, figure 1. The covering layer was initially stored in a desiccator with distilled water to ensure dissolution of any salts present prior to placing the sample below a stereomicroscope (SMZ25 NIKON with NIS-Elements D software) at drier lab conditions. Using the microscope software for accurately measuring layering distances, displacement of one layer (not the surface layer) was indicated within a short timeframe (< 2 hours) which stresses the layering. This crystallization reaction time is consistent with the timeframe found in (Godts et al. 2020) for one NaCl crystal (30 minutes, RH 90%→RH 70%).

Figure 1. Unpolished cross section from the wall painting covering layer, Magleby Church Denmark. From the bottom, the contact surface with the original wall painting and towards the top of the picture still newer added layers.

KNOWLEDGE GAP

Many conservation projects will require consolidation, but knowledge of the influence that salt kinetics may have on the applied consolidant is missing. This is a critical point that needs to be addressed prior to uncovering this valuable cultural heritage, as e.g. uncovering of the second vault in Rørby. A new measuring methodology allows detection of salts following the actual deliquescence RH of the salt mixture based on microsamples (< 25 mg) (Rörig-Dalgaard 2021) and is therefore also applicable on plaster layers. This new measuring methodology could be used to fill this knowledge gap if extended with research including kinetics.

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