Case Studies in Construction Materials 17 (2022) e01501

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Case study

Coating's influence on wind erosion of porous stones used in the Cultural Heritage of Southern Italy: Surface characterisation and resistance

Raffaella Striani [a], Marta Cappai [b], Ludovica Casnedi [b], Carola Esposito Corcione [a,*], Giorgio Pia [b]

[a] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, 73100 Lecce, Italy
[b] Dipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Università di Cagliari, via Marengo 2, 09123 Cagliari, Italy

ARTICLE INFO

Keywords:
Conservation
Limestone
Photopolymerizable protective coating
Organic-Inorganic hybrids
Erosion
Sandblasting

ABSTRACT

Wind erosion (or aeolian corrosion) is one of the most relevant causes of weathering and degradation which has affected building surfaces in Cultural Heritage. The effect depends on the wind strength, the impact of particles transported and their size and the characteristics of surfaces affected. This aspect is very important for historical buildings constructed by using limestone as Lecce stone (LS). LS has an extraordinary ability to be shaped, but is very sensitive to decay. Exfoliation, wind erosion, absorption of water by capillary from the soil, are its main degradation causes. For such a reason, the application of effective products able to act as "sacrifice film" became necessary in order to minimise the degradation rate by preserving the limestone substrate against serious weathering agents. In this work, the effects of aeolian corrosion, simulated by means the accelerated test with sandblasting method, were studied. In particular, the effectiveness of two specific commercial coatings, such as an innovative free-solvent hybrid organic-inorganic coating (HYBRID) and a solvent-based coating (AS), was assessed relating to their capability to preserve Lecce stone from the aeolian corrosion phenomenon. The protective efficacy was guaranteed by both the commercial coatings even after accelerated wind erosion test, by confirming a high hydrophobicity, low capillary water absorption and an adequate depth of penetration inside the stone able to assure durability.

1. Introduction

Porous limestone is one of the most used building materials in the Cultural Heritage for millennia and continue to be extensively used as cladding and building material due to its load-bearing capacity. Countless historic cities were built using this sedimentary rock thanks to its easy availability and workability. Many examples of its use can be found in Europe [1–3] and throughout the Mediterranean basin [4,5]. In Italy, it is used in the entire territory and there are significant examples especially in Sicily [6,7], Apulia [8], Sardinia [9,10] and Basilicata [11,12].

In the past, the limestone was considered resistant and durable, but over time it has been realised that it was particularly susceptible to atmospheric agents, thus specific protective and conservation treatments are required [13,14].

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* Corresponding author.
E-mail address: carola.corcione@unisalento.it (C. Esposito Corcione).

https://doi.org/10.1016/j.cscm.2022.e01501
Received 20 July 2022; Received in revised form 16 September 2022; Accepted 20 September 2022

Rainwater, wind, thermal-hygrometric variations and anthropogenic environmental agents are the principal causes of stone made monuments' deterioration, which lead to the dissolution and aesthetic value loss of the material. The action of water capillary absorption with other environmental factors may lead to salt crystallisation, wet-dry and freeze-thaw cycles [15–18], biological colonisation and acid rain effects [3,19]. The level of weathering depends on intrinsic properties of building stone and the geographical monument location [20].

For example, in semiarid and desert areas, one of most typical mechanisms of deterioration is the movement and consequent impact of particles of sand on the stone surface [21–23]. The sand, transported by wind and moved by *saltation*, impacts the material stressing the surfaces which generate progressively micro cracks and material loss [21,24]. This phenomenon, knows as aeolian corrosion, is influenced by many aspects including extrinsic conditions, like the typology of particles (size, shape and hardness), the wind velocity and directionality, and intrinsic characteristics like surface material composition, its mechanical resistance, morphological aspect and moisture condition [25–29]. Indeed, moisture is one of the most important parameters to be taken into account because it is involved in the electrochemical and inter-particle surface forces (adhesive forces). A confirmation of aeolian corrosion is more aggressive on the windy day, when the water absorbed by the material is lesser (and consequently cohesion force) and the detachment of the granules is visible [22].

In order to preserve and minimise the degradation of Cultural Heritage, the most widely used methods of superficial protection include the application of protectives to give hydrophobicity to the surface of the material [30–34] and the use of consolidating agents to restore and increase grain cohesion and surface strength without modifying other physical features of the limestone [35–37].

Several organic, inorganic and HYBRID products have been used for this purpose. Starting from the 1960s, due to their optical characteristics (transparency) and water repellent effect, acrylic and methacrylic monomers have been commonly used in the cultural heritage preservation playing a remarkable role as consolidating and protecting material [38]. However, over time, acrylic systems have shown poor durability due to their tendency to photo-oxidise when exposed to a slow and serious weathering. In addition, even if they can be considered irreversible treatments, they present a good re-treatability [39,40]. On the other hand, inorganic protective coatings were usually applied for their compatibility with the substrate, good durability and reversibility. However, they present a few weaknesses such as intrinsic fragility, low mechanical properties and poor penetration inside the treated substrate [32].

In the previous works [32,41–43], the authors developed organic-inorganic (O-I) methacrylic-based photopolymerizable hydrophobic protectives for different kinds of substrates. The possibility of achieving a superhydrophobic behaviour of the treated stone in a very short time and a very low environmental impact are some of the most evident advantages of these innovative coatings. In particular, a photopolymerizable organic-inorganic hybrid product was developed and deeply studied as protective coating for porous stones. All the protective performances of the hybrid product were evaluated in terms of: hydrophobicity, colorimetry, capillary water absorption, transmission degree of liquid water, transmission degree of water vapour, durability. The details are reported in previous works [32,44,45] in comparison with high quality commercial protective products. The hybrid coating was, successively, patented and commercialised, as specified in the Experimental section.

The present paper describes an extensive investigation intended at measuring, by means of the accelerate aging sandblasting tests, the effectiveness of the organic-inorganic hybrid coating and a commercial protective on a typical Apulia limestone substrate (Lecce Stone, LS). The purpose is to propose an approach based on the quantification of the influence of sand particles on the strength of the surface, which can be used as an instrument to validate the suitability of coatings.

2. Experimental

2.1. Stone substrate: Lecce Stone (LS)

The selected porous stone was Lecce Stone, the typical calcarenitic lithotype of South-East Italian region (Apulia-Salento). It is composed of bioclasts of around 150 μm, phosphatic nodules and a large number of little glauconite grains; the micritic matrix is composed of clay minerals. General data for this stone report a considerable pore fraction which is about 0.36. The approximate interconnected pore size ranges from 0.01 μm to 30 μm and the average dimension of pores is around 1 μm [44].

2.2. Application of commercial products on Lecce Stone (LS)

The coatings influence evaluation of wind erosion of Lecce Stone has been performed by using two high quality commercial protective products:

- Antipluviol S (labelled hereinafter as AS), supplied by MAPEI, is a transparent solvent-based product composed of silane and siloxane, suitable for different construction materials. As reported in the technical datasheet [46], AS creates an efficient protective coating, hydrophobic, and is able to penetrate inside the substrate, capable of reducing biological colonisation by mosses and algae. This product is also strongly resistant to UV radiations and alkaline environments. LS samples have been coated with4 to 5 subsequent layers (wet on wet by brush) using AS in a quantity between 0.01 and 0.08 g/cm^2 per hand, as suggested by the supplier. By considering the typology of the product, since it is a solvent-based coating, formed by more than 90 % of solvent and less than 10 % by the active substance, with the evaporation of the solvent the coating is formed by means of the coalescence (physical phenomenon). For such a reason, a higher quantity of product is required during the application in order to guarantee a uniform treatment.

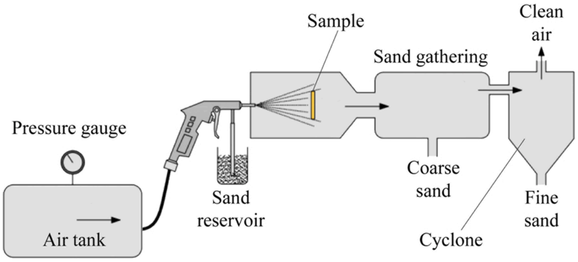

Fig. 1. Schematic drawing of experimental device for measuring abrasion resistance.

- HYBRID, developed and patented in Europe by some of the authors of the University of Salento and currently supplied by Linea Copernico of DELL'ANNA MUIA S.u.r.l. It is an innovative water-repellent photopolymerizable nanostructured Organic-Inorganic product for the protection of fair-faced walls in natural stone, artificial stone and concrete. The product is composed of organic domains, based on silanes and siloxanes, strongly interconnected with an inorganic nanoscale structure, ensuring a highly water-repellent, breathable and transparent effect in only a few hours in the absence of solvents. An amount of 0.04 g/cm^2 of HYBRID was applied to LS specimens in a single hand by brush and then the coated samples were exposed to sunlight for 55 h [45,47]. HYBRID is a free-solvent photopolymerizable product, able to create a coating by means of chemical reactions following the absorption of solar radiations by active substances (photoinitiators) able to activate the radical photopolymerization, as studied in a previous work [48]. HYBRID is constituted of 95 % of active substance (organic fraction), this means that the quantity of product applied on the stone is totally reactive with the great advantage to obtain the maxima yield, instead, the 5 % of inorganic fraction guarantee a compatibility with the mineral nature of the limestone by conferring a mechanical improvement.

Before any application of the commercial products, the LS specimens were cleaned and prepared in agreement with UNI EN 16581:2015 [49]. At least three samples were used for each test.

2.3. Experimental techniques

Sandblasting tests were performed on untreated and treated LS samples using the device shown in Fig. 1.

The exposed squared surface has a side length equal to 70 mm, while the thickness of the samples is 10 mm. Abrasive material is a quartz sand composed of particle size diameter of 900 μm. Nozzle is positioned at 28 cm from the sample which has been blasted for 1 min (at a pressure of 2 bar). This procedure was repeated 25 times. At the end of each cycle, weight loss was measured and the morphological characteristics of erosion were evaluated by observing images obtained by scanning blasted surfaces.

Air velocity profile was measured using the Hot Wire Anemometer HHF-SD1 by Omega, while a professional dynamometer connected to the target plate was used for determining the impact force.

SEM analyses (Zeiss Evo40), were performed to assess the result of the erosion aging test on the surface characteristics and morphology of the coated and uncoated stone. The combination of SEM and EDS techniques allowed to obtain more information about aging by considering specific composition by elemental analyses, in particular the concentration and the distribution of each element within the stone.

The hydrophobicity of the untreated and treated stone elements before and after accelerated erosion test was performed by means of a First Ten Angstroms FTA1000 Quick Start instrument, furnished with a video-camera. The investigations were made by using the sessile drop technique with (at room temperature) bi-distilled water (surface tension $\gamma = 72.1$ mN/m), following the instructions of NORMAL Protocol 33/89 [50]. Ten experiments were carried out on each sample before and after the aging test. All the results were averaged.

Capillary water absorption ability, by using gravimetric sorption procedure, was assessed on untreated and treated stone samples (120 × 60 × 10 mm), after the accelerated erosion test, according to UNI 15801:2010 [51]. The preserved surface of each sample was placed on a filter paper pad (around 1 cm thick), wetted with distilled water. The wet specimen mass, m_i, was defined by measuring the weight of each sample after 10, 20 and 30 min and 1,4, 6, 24, 48, 96 h up to 8 days. As recommended by Normal UNI 15801:2010 [51], the quantity of absorbed water per unit area, Q_i (mg/cm^2) is:

$$Qi = \left(\frac{m_i - m_0}{A}\right)1000 \tag{1}$$

where: m_i is the sample mass (g) at the time t_i(s), m_0 is the dry mass of each sample (g) and A is the surface area exposed to wet pad (cm^2). Q_i values were plotted vs. square root of time (s$^{1/2}$) according to:

$$Q = K \bullet t^{1/2} \tag{2}$$

where: Q represents the absorbed water, K is a proportional constant and t is time (s) to give the capillary absorption curve.

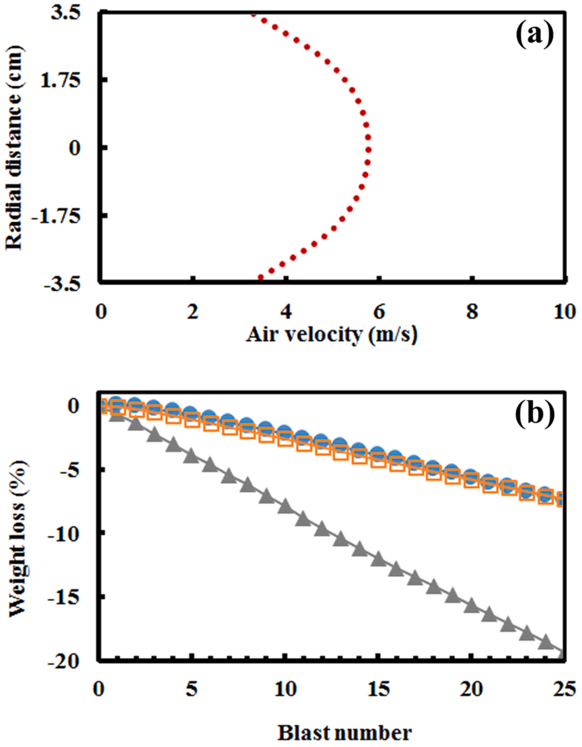

Fig. 2. a) Air velocity profile with the sample at 28 cm from the nozzle, air pressure: 2 bar pressure; b) abrasion (g/m^2 min) of the LS_NT (▲), LS_AS (●) and LS_HYBRID (□).

Fig. 3. LS_NT, LS_ HYBRID and LS_AS samples during erosion test.

3. Results and discussion

The study of the erosion process highlights untreated and treated LS samples' resistance to the effects of a serious and slow weathering, principally due to the wind action. Nozzle distance and air pressure have been selected for simulating a moderate breeze; Beaufort scale value equal to 4 and air velocity of about 5.77 m/s (20.77 km/h). It is evident from Fig. 2a, that this condition, besides being very common, gives the possibility to have a constant and approximately homogenous impact process on the entire surface [52].

Preliminary tests allow estimating: (i) the reduction in air pressure, when sand is introduced into the airstream, from 37 N/m^2 (for air) alone to 28 N/m^2 (for air + sand); (ii) the quantity of sand which hits samples surface of about 142.85 g/min; and (iii) the number of grains calculated taking into account their spherical volume ($V = \frac{4}{3}\pi r^3$) and Quartz specific weight (2.5 g/cm^3) which consists of about 150k at the 2 bar pressure.

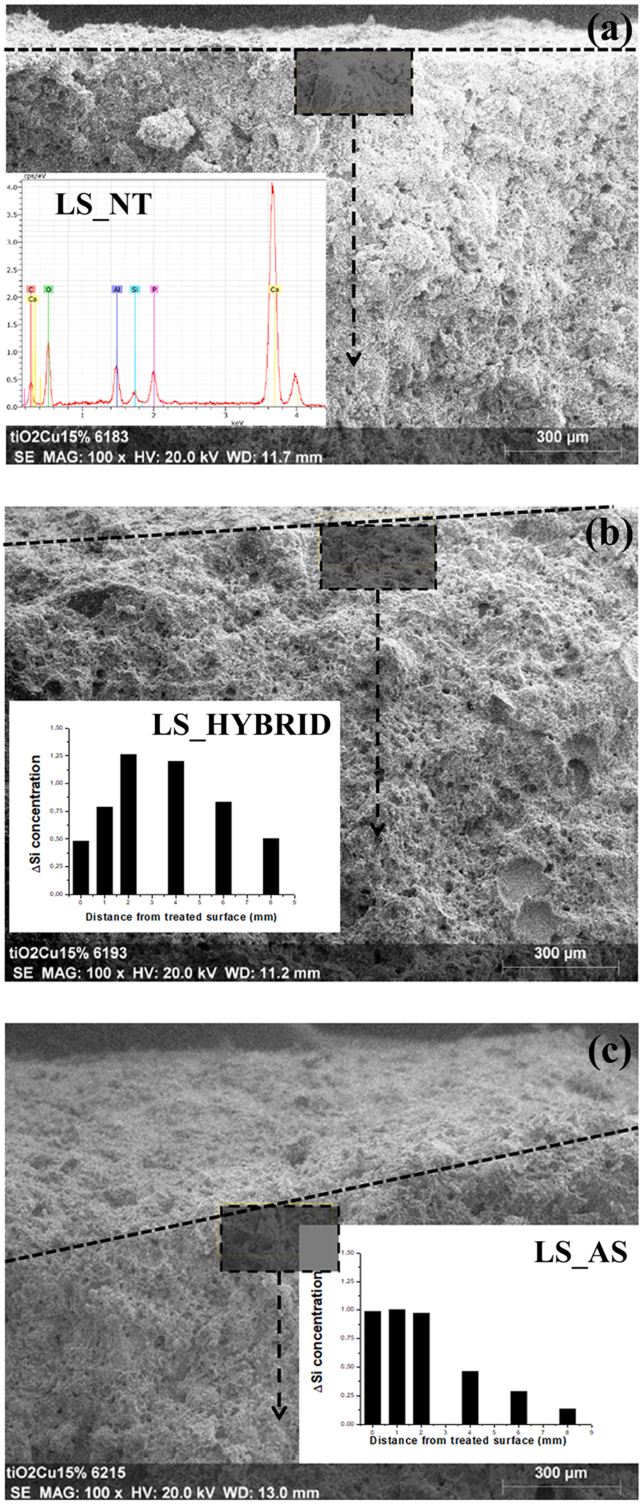

Fig. 4. SEM images of untreated and treated stone after aging test. a) LS_NT; b) LS_HYBRID; c) LS_AS.

The abrasion of untreated and treated stone specimens is expressed in terms of weight reduction percentage. As expected, LS untreated shows a larger mass loss than samples which are treated with a specific coating. In particular, the weight loss percentage after 25 cycles is equal to 19.33 ± 0.45 %, while for LS treated with the AS and HYBRID coatings it is equal to 7.44 ± 0.34 % and 7.35 ± 0.38 % respectively (Fig. 2b). It is evident that the values for LS_AS and LS_H are very similar, but the difference is in the morphology

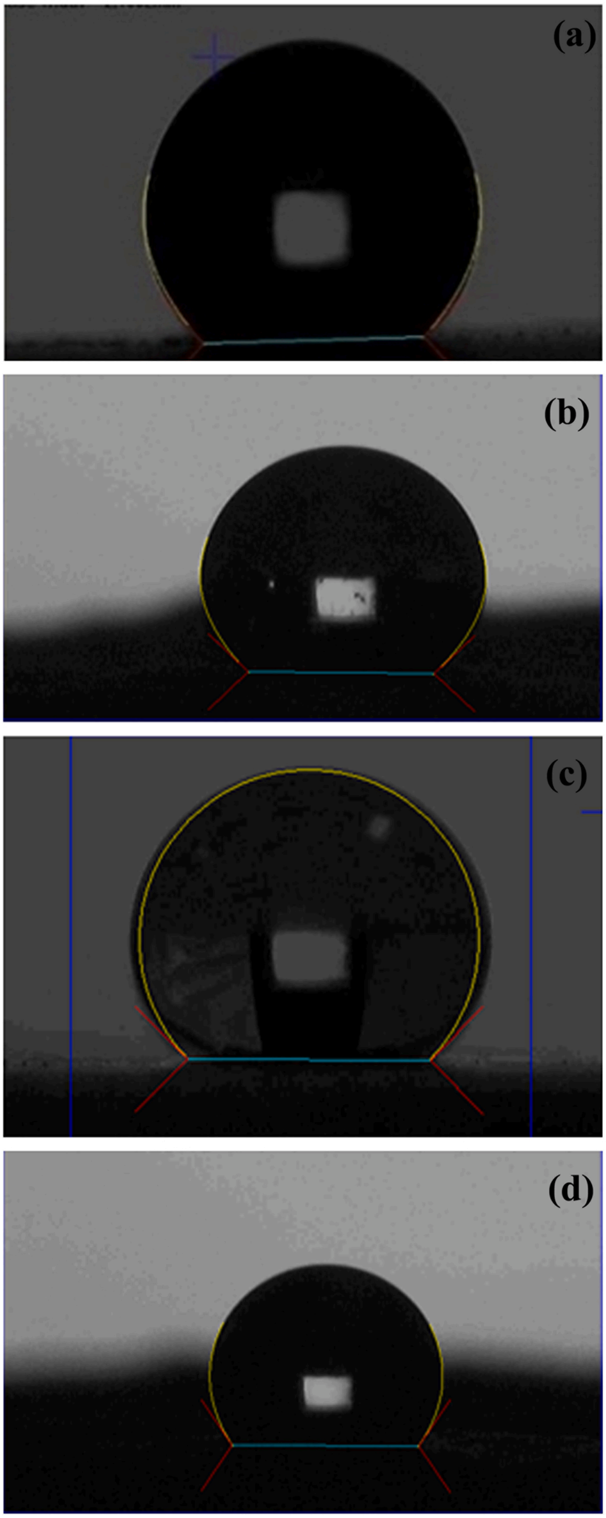

Fig. 5. Contact angle measurements on LS treated with experimental and commercial products. a) LS_HYBRID before accelerated erosion test α = (135.1 ± 1.2)°; b) LS_HYBRID after accelerated erosion test α = (135.1 ± 2.8)°; a) LS_AS before accelerated erosion test α = (135.4 ± 1.9)°; b) LS_AS after accelerated erosion test α = (126.1 ± 3.6)°.

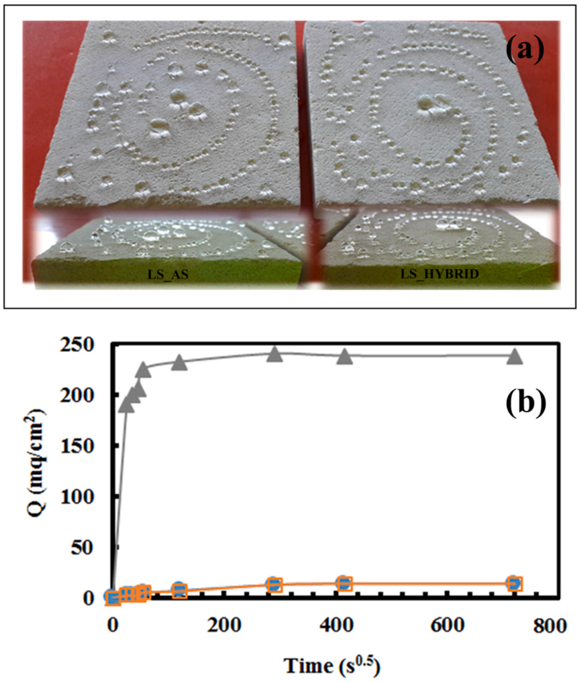

Fig. 6. Capillary test after surface erosion. Sorption curves of LS untreated (▲), LS treated with the AS (•) and HYBRID (☐) coatings with the corresponding pictures after the capillarity test.

of decay. Indeed, HYBRID coating seems to protect uniformly the entire surface than AS. These last samples present a relevant degradation in correspondence with the maximum value of air-sand flow velocity (Fig. 3).

In this last figure, it can be noted that the treatment with HYBRID and AS coatings are particularly effective. Cohesive capability of used coatings minimises the abrasive effect by 3 times the initial value.

SEM was employed to examine the LS face treated with both commercial products. The resulting micrographies, with the corresponding EDS analyses, of the coated and uncoated LS samples, after the accelerated erosion test, are reported in Fig. 4.

Each SEM micrography shows a regular dispersal of each coating on the observed surface, showing the lack of imperfections and gaps. In addition, the erosion effect of the surface is more evident for untreated stone and slightly noticeable for LS treated with HYBRID. The most important components achieved by EDS analyses are visible in the inset of Fig. 4a for untreated stone. The same qualitative EDS spectrum was obtained for the treated stone specimens, showing that both uncoated and coated LS surfaces comprehend, as expected for calcarenitic limestones, calcium, silicon and carbon. Since the commercial products contained silane and siloxane, the EDS estimated the quantity of silicon (obtained eliminating the amount of Si due to the untreated stone) considering the distance from the outside surface of the substrate in order to estimate the penetration depth of the coatings. A slight abstraction of the HYBRID coating from the external surface of the stone was registered due to the accelerated erosion test. However, a high penetration depth of about 8 mm (see inset of Fig. 4b) was measured for the HYBRID coating, evidencing the presence of HYBRID on the external and the inner surface of the stone. Referring to the solvent-based product (see inset of Fig. 4c), the EDS analysis evidences that AS possesses a high penetration depth of about 8 mm, evidencing, in addition, a higher amount of the product on the external surface of the stone, even though it was exposed to the aging treatment. The presence of both commercial coatings inside the stone represents an important direct evidence of their excellent protective properties and durability, since both of them were not completely removed from the stone due to the accelerated erosion aging test.

In order to determine if the aging treatment influenced the super-hydrophobic performances of both commercial products, several measurements of contact water angle were, hence, made on uncoated and coated LS stone after the erosion experimental measurements. The results were compared with that obtained on the treated stone before the erosion tests (Fig. 5).

The measurements performed on untreated stone are not reported because the contact angle tests were unsuccessful due to the ultra-rapid absorption of the water droplet. On the other hand, the presence of both coatings conveys an excellent superficial hydrophobicity to the stone, witnessed by a contact angle much higher than 90°, which remains almost unchanged even after the erosion test. In detail, the water contact angle registered for HYBRID coating was about 135° before and after the aging test, while the contact angle measured for the commercial product AS slightly decreased from about 135° to about 126°. Both results are an important evidence of the capability of the products to protect the surface of the stone from liquid water absorption, even in extreme outdoor conditions, confirming their outstanding protective properties and durability. The contact angle results represent, in turn, indirect evidence of the presence of the products, even on the stone surface, after the accelerated erosion test, according to the SEM/EDS results, reported in Fig. 5.

The measurements of water capillary absorption were obtained for untreated and treated aged stone samples as reported in Fig. 6.

The water capillary curves validate that both HYBRID and AS products are able to ensure excellent comparable hydrophobicity to the calcarenite stone, still following severe aging conditions.

The picture reported in the inset of Fig. 6, performed on the treated stone samples after both erosion and capillarity tests, still evidences an exceptional durability of the protectives properties of both HYBRID and AS coatings, which continue to preserve the stone surface from the liquid water, regardless of the simultaneous reproduction of two particularly damaging atmospheric agents, such as erosion and water capillary increase.

4. Conclusion

Cultural Heritage preservation is one of the most important issues for scientific research applied to building materials. In this sense, the effect of a serious and slow weathering due to wind erosion is characterised by a complex process which depends on extrinsic and intrinsic causes. For these reasons, the investigated solution is focused on the proper coatings which are able to protect exposed surface without altering general and specific properties.

In this paper, an accelerated wind erosion procedure has been applied to untreated and treated specimens. The application of small amounts of the innovative HYBRID coating on the calcarenitic stone surface conferred an extraordinary and durable hydrophobicity to the selected porous stone, able to assurance a very high protection of the stone from water, even after a severe erosion simulation test. In conclusion, the HYBRID product is able to equate the properties of the commercial AS product, with the further benefit to be eco-friendly, avoiding the use of harmful solvents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

References

[1] J. Cassar, The use of limestone in a historic context – the experience of malta, Geol. Soc. Spec. Publ. 331 (2010) 13–25, https://doi.org/10.1144/SP331.2.

[2] S. Siegesmund, W.D. Grimm, H. Dürrast, J. Ruedrich, Limestones in Germany used as building stones: an overview, Geol. Soc. Spec. Publ. 331 (2010) 37–59, https://doi.org/10.1144/SP331.4.

[3] A.C. Pinheiro, N. Mesquita, J. Trovão, F. Soares, I. Tiago, C. Coelho, H.P. de Carvalho, F. Gil, L. Catarino, G. Piñar, A. Portugal, Limestone biodeterioration: a review on the Portuguese cultural heritage scenario, J. Cult. Herit. 36 (2019) 275–285, https://doi.org/10.1016/j.culher.2018.07.008.

[4] J.P. Calvo, M. Regueiro, Carbonate rocks in the mediterranean region – from classical to innovative uses of building stone, Geol. Soc. Spec. Publ. 331 (2010) 27–35, https://doi.org/10.1144/SP331.3.

[5] K. Zoghlami, J.D. Martín-Martín, D. Gómez-Gras, A. Navarro, D. Parcerisa, J.R. Rosell, The building stone of the Roman city of Dougga (Tunisia): provenance, petrophysical characterisation and durability, Comptes Rendus - Geosci. 349 (2017) 402–411, https://doi.org/10.1016/j.crte.2017.09.017.

[6] M.F. La Russa, C.M. Belfiore, G.V. Fichera, R. Maniscalco, C. Calabrò, S.A. Ruffolo, A. Pezzino, The behaviour to weathering of the Hyblean limestone in the Baroque architecture of the Val di Noto (SE Sicily): an experimental study on the “calcare a lumachella” stone, Constr. Build. Mater. 77 (2015) 7–19, https://doi.org/10.1016/j.conbuildmat.2014.11.073.

[7] C.M. Belfiore, C. Calabrò, S.A. Ruffolo, M. Ricca, Török, A. Pezzino, M.F. La Russa, The susceptibility to degradation of stone materials used in the built heritage of the Ortygia island (Syracuse, Italy): a laboratory study, Int. J. Rock Mech. Min. Sci. 146 (2021), https://doi.org/10.1016/j.ijrmms.2021.104877.

[8] A. Merico, R. Bellopede, A. Fiorucci, P. Marini, Itria Valley (Apulia, Italy): comparison of limestones for the construction and restoration of “Trulli” roofing, Resour. Policy 76 (2022), 102630, https://doi.org/10.1016/j.resourpol.2022.102630.

[9] G. Pia, L. Casnedi, R. Ricciu, L.A. Besalduch, O. Cocco, A. Murru, P. Meloni, U. Sanna, Thermal properties of porous stones in cultural heritage: experimental findings and predictions using an intermingled fractal units model, Energy Build. 118 (2016) 232–239, https://doi.org/10.1016/j.enbuild.2016.03.011.

[10] G. Pia, C. Siligardi, L. Casnedi, U. Sanna, Pore size distribution and porosity influence on Sorptivity of ceramic tiles: from experimental data to fractal modeling, Ceram. Int. (2016), https://doi.org/10.1016/j.ceramint.2016.03.041.

[11] F.T. Gizzi, M. Sileo, M. Biscione, M. Danese, M. Alvarez de Buergo, The conservation state of the Sassi of Matera site (Southern Italy) and its correlation with the environmental conditions analysed through spatial analysis techniques, J. Cult. Herit. 17 (2016) 61–74, https://doi.org/10.1016/j.culher.2015.05.002.

[12] A.E. Bonomo, A. Minervino Amodio, G. Prosser, M. Sileo, G. Rizzo, Evaluation of soft limestone degradation in the Sassi UNESCO site (Matera, Southern Italy): loss of material measurement and classification, J. Cult. Herit. 42 (2020) 191–201, https://doi.org/10.1016/j.culher.2019.07.017.

[13] B.J. Smith, M. Gomez-Heras, H.A. Viles, Underlying issues on the selection, use and conservation of building limestone, Geol. Soc. Spec. Publ. 331 (2010) 1–11, https://doi.org/10.1144/SP331.1.

[14] C. Genestar, C. Pons, J.C. Cerro, V. Cerdà, Different decay patterns observed in a nineteenth-century building (Palma, Spain), Environ. Sci. Pollut. Res. 21 (2014) 8663–8672, https://doi.org/10.1007/s11356-014-2761-7.

[15] M.A. Hassine, K. Beck, X. Brunetaud, M. Al-Mukhtar, Strain measurements during capillary water infiltration in porous limestones, Constr. Build. Mater. 175 (2018) 439–447, https://doi.org/10.1016/j.conbuildmat.2018.04.182.

[16] C. Cardell, D. Benavente, J. Rodríguez-Gordillo, Weathering of limestone building material by mixed sulfate solutions. Characterization of stone microstructure, reaction products and decay forms, Mater. Charact. 59 (2008) 1371–1385, https://doi.org/10.1016/j.matchar.2007.12.003.

[17] R. Bellopede, E. Castelletto, P. Marini, Ten years of natural ageing of calcareous stones, Eng. Geol. 211 (2016) 19–26, https://doi.org/10.1016/j.enggeo.2016.06.015.

[18] T.C. Chen, M.R. Yeung, N. Mori, Effect of water saturation on deterioration of welded tuff due to freeze-thaw action, Cold Reg. Sci. Technol. 38 (2004) 127–136, https://doi.org/10.1016/j.coldregions.2003.10.001.

[19] C.C. Gaylarde, P.M. Gaylarde, A comparative study of the major microbial biomass of biofilms on exteriors of buildings in Europe and Latin America, Int. Biodeterior. Biodegrad. 55 (2005) 131–139, https://doi.org/10.1016/j.ibiod.2004.10.001.

[20] B. Sena da Fonseca, A.P. Ferreira Pinto, A. Rodrigues, S. Piçarra, M.F. Montemor, The role of properties on the decay susceptibility and conservation issues of soft limestones: Contribution of Ançã stone (Portugal), J. Build. Eng. 44 (2021), 102997, https://doi.org/10.1016/j.jobe.2021.102997.

[21] D. Camuffo, Controlling the aeolian erosion of the Great Sphinx, Stud. Conserv. 38 (1993) 198–205, https://doi.org/10.2307/1506380.

[22] D. Camuffo, Physical weathering of stones, Sci. Total Environ. 167 (1995) 1–14, https://doi.org/10.1016/0048-9697(95)04565-I.

[23] J. Martínez-Martínez, D. Benavente, S. Jiménez Gutiérrez, M.A. García-del-Cura, S. Ordóñez, Stone weathering under Mediterranean semiarid climate in the fortress of Nueva Tabarca Island (Spain), Build. Environ. 121 (2017) 262–276, https://doi.org/10.1016/j.buildenv.2017.05.034.

[24] J.E. Laity, N.T. Bridges, Abraded Systems, Elsevier Ltd., 2013, https://doi.org/10.1016/B978-0-12-374739-6.00307-9.

[25] C. Atzeni, F. Bodano, U. Sanna, N. Spanu, Surface strength: definition and testing by a sand impact method, J. Cult. Herit. 7 (2006) 201–205, https://doi.org/10.1016/j.culher.2006.05.002.

[26] C. Atzeni, G. Pia, U. Sanna, N. Spanu, Surface wear resistance of chemically or thermally stabilized earth-based materials, Mater. Struct. 41 (2008) 751–758, https://doi.org/10.1617/s11527-007-9278-1.

[27] X. Cai, Z. He, S. Tang, X. Chen, Abrasion erosion characteristics of concrete made with moderate heat Portland cement, fly ash and silica fume using sandblasting test, Constr. Build. Mater. 127 (2016) 804–814, https://doi.org/10.1016/j.conbuildmat.2016.09.117.

[28] Q. Chen, D.Y. Li, Computer simulation of solid particle erosion, Wear 254 (2003) 203–210, https://doi.org/10.1016/S0043-1648(03)00006-1.

[29] M. Cappai, L. Casnedi, G. Carcangiu, F. Delogu, D. Pozzi-escot, G. Pacheco, G. Pia, P. Meloni, Weathering of earth-painted surfaces: environmental monitoring and artificial aging, Constr. Build. Mater. 344 (2022), 128193, https://doi.org/10.1016/j.conbuildmat.2022.128193.

[30] G. Cappelletti, P. Fermo, Hydrophobic and Superhydrophobic Coatings for Limestone and Marble Conservation, Elsevier Ltd, 2016, https://doi.org/10.1016/B978-1-78242-283-9.00015-4.

[31] D. Colangiuli, A. Calia, N. Bianco, Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage, Constr. Build. Mater. 93 (2015) 189–196, https://doi.org/10.1016/j.conbuildmat.2015.05.100.

[32] G. Pia, C. Esposito Corcione, R. Striani, L. Casnedi, U. Sanna, Coating's influence on water vapour permeability of porous stones typically used in cultural heritage of Mediterranean area: experimental tests and model controlling procedure, Prog. Org. Coat. 102 (2017) 239–246, https://doi.org/10.1016/j.porgcoat.2016.10.021.

[33] M. Torabi-Kaveh, M. Moshrefyfar, S. Shirzaei, S.M.A. Moosavizadeh, B. Ménendez, S. Maleki, Application of resin-TiO_2 nanoparticle hybrid coatings on travertine stones to investigate their durability under artificial aging tests, Constr. Build. Mater. 322 (2022), 126511, https://doi.org/10.1016/j.conbuildmat.2022.126511.

[34] S. Raneri, G. Barone, P. Mazzoleni, I. Alfieri, L. Bergamonti, T. De Kock, V. Cnudde, P.P. Lottici, A. Lorenzi, G. Predieri, E. Rabot, J. Teixeira, Efficiency assessment of hybrid coatings for natural building stones: advanced and multi-scale laboratory investigation, Constr. Build. Mater. 180 (2018) 412–424, https://doi.org/10.1016/j.conbuildmat.2018.05.289.

[35] P. Maravelaki-Kalaitzaki, N. Kallithrakas-Kontos, D. Korakaki, Z. Agioutantis, S. Maurigiannakis, Evaluation of silicon-based strengthening agents on porous limestones, Prog. Org. Coat. 57 (2006) 140–148, https://doi.org/10.1016/j.porgcoat.2006.08.007.

[36] E. Sassoni, E. Franzoni, B. Pigino, G.W. Scherer, S. Naidu, Consolidation of calcareous and siliceous sandstones by hydroxyapatite: comparison with a TEOS-based consolidant, J. Cult. Herit. 14 (2013) e103–e108, https://doi.org/10.1016/j.culher.2012.11.029.

[37] E. Vasanelli, A. Calia, M. Masieri, G. Baldi, Stone consolidation with SiO_2 nanoparticles: effects on a high porosity limestone, Constr. Build. Mater. 219 (2019) 154–163, https://doi.org/10.1016/j.conbuildmat.2019.05.169.

[38] M.K. Khallaf, A.A. El-Midany, S.E. El-Mofty, Influence of acrylic coatings on the interfacial, physical, and mechanical properties of stone-based monuments, Prog. Org. Coat. 72 (2011) 592–598, https://doi.org/10.1016/j.porgcoat.2011.06.021.

[39] A. Artesani, F. Di Turo, M. Zucchelli, A. Traviglia, Recent advances in protective coatings for cultural, Coatings 10 (2020).

[40] C. Esposito Corcione, N. De Simone, M.L. Santarelli, M. Frigione, Protective properties and durability characteristics of experimental and commercial organic coatings for the preservation of porous stone, Prog. Org. Coat. 103 (2017) 193–203, https://doi.org/10.1016/j.porgcoat.2016.10.037.

[41] C. Esposito Corcione, R. Striani, M. Frigione, Organic-inorganic UV-cured methacrylic-based hybrids as protective coatings for different substrates, Prog. Org. Coat. 77 (2014) 1117–1125, https://doi.org/10.1016/j.porgcoat.2014.03.010.

[42] C. Esposito Corcione, R. Striani, M. Frigione, Sunlight curable hybrid organic-inorganic methacrylic-based coatings: analysis of the cure mechanism and functional properties, Polym. Adv. Technol. 26 (2015) 167–175, https://doi.org/10.1002/pat.3445.

[43] G. Pia, C. Esposito Corcione, R. Striani, L. Casnedi, U. Sanna, Thermal conductivity of porous stones treated with UV light-cured hybrid organic-inorganic methacrylic-based coating. Experimental and fractal modeling procedure, Prog. Org. Coat. 94 (2016) 105–115, https://doi.org/10.1016/j.porgcoat.2016.02.013.

[44] R. Striani, C. Esposito Corcione, G. Dell'Anna Muia, M. Frigione, Durability of a sunlight-curable organic–inorganic hybrid protective coating for porous stones in natural and artificial weathering conditions, Prog. Org. Coat. 101 (2016) 1–14, https://doi.org/10.1016/j.porgcoat.2016.07.018.

[45] C. Esposito Corcione, R. Striani, M. Frigione, Novel hydrophobic free-solvent UV-cured hybrid organic-inorganic methacrylic-based coatings for porous stones, Prog. Org, Coatings 77 (2014) 803–812, https://doi.org/10.1016/j.porgcoat.2014.01.008.

[46] MAPEI, Antipluviol S – Technical Data Sheet 327-11-2009-II-gb, 2009. 〈https://cdnmedia.mapei.com/docs/librariesprovider2/products-documents/1_00327_antipluviol-s_it-it_024ae14022e9424a99b263bd3c4bb37a.pdf?sfvrsn=37d593fa_0〉.

[47] R. Striani, C. Esposito Corcione, G. Dell'Anna Muia, M. Frigione, Durability of a sunlight-curable organic–inorganic hybrid protective coating for porous stones in natural and artificial weathering conditions, Prog. Org. Coat. 101 (2016) 1–14, https://doi.org/10.1016/j.porgcoat.2016.07.018.

[48] C.E. Corcione, R. Striani, M. Frigione, UV-cured methacrylic-silica hybrids: effect of oxygen inhibition on photo-curing kinetics, Thermochim. Acta 576 (2014) 47–55, https://doi.org/10.1016/j.tca.2013.11.028.

[49] UNI EN 16581:2015, Conservation of Cultural Heritage – surface protection for porous inorganic materials – laboratory test methods for the evaluation of the performance of water repellent products, 2015.

[50] Normal Protocol 33/89, Contact Angle Determinations, 1993.

[51] UNI, UNI EN 15801 – conservation of cultural property – test methods – determination of water absorption by capillarity, 2010.

[52] P. Chevallier, A.B. Vannes, Effects on a sheet surface of an erosive particle jet upon impact, Wear 184 (1995) 87–91, https://doi.org/10.1016/0043-1648(94)06562-4.