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Efficiency assessment of hybrid coatings for natural building stones: Advanced and multi-scale laboratory investigation

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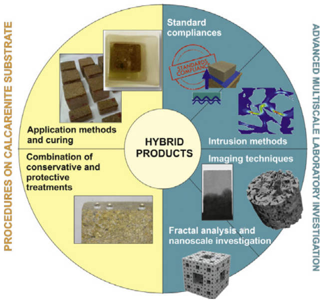
HIGHLIGHTS

- Efficiency of hybrid coatings were assessed on calcarenite substrate by using several techniques.
- Advantages and limitations of classic and innovative methods were highlighted.
- Al-Si-based product led to changes not advisable for calcarenite substrates.
- Polyamidoamine-based product is more suitable for porous calcarenite consolidation.
- Merits and limitations of the hydrophobic coating used in combination with consolidants were explored.

GRAPHICAL ABSTRACT



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ABSTRACT

The efficiency of a hybrid patented consolidant (PAASi) and two commercially available hybrid coatings (a consolidant named AlSiX and a hydrophobic product named WS3) properly modified was assessed on a calcarenite substrate. Test routines based on standard recommendations were first applied to evaluate the performances of the consolidant and protective treatments, while the investigation of additional aspects such as penetration depth and interaction with the substrate was achieved by a multi-scale approach based on classic intrusion methods (mercury intrusion porosimetry) and Drilling Resistance Measurement System (DRMS), combined with non-invasive imaging techniques (X-ray computed micro-tomography and neutron radiography) and small angle neutron scattering (SANS). A distinct interaction of the products with the pore network of the stone was quantified in the range 0.007–200 μm. Their effects on capillary water absorption were also visualized with neutron imaging. The suitability of the products on the selected substrate was discussed, highlighting also how the applied routine can support conservation material studies. The results indicated that the Al-Si-based product led to unwanted effects. Alternative application methods and/or curing procedures have to be explored to overtake these undesirable changes. On the contrary, the polyamidoamine-based product seemed to be more suitable for

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calcarenite substrates conservation. The performances of the hydrophobic coating, when used in combination with consolidants, were strictly influenced by the pre-consolidation of the substrate.

1. Introduction

One of the main difficulties in conservation field is the choice of suitable consolidants and protective treatments for stones, able to preserve masonry, compatible with the stone substrate of interest, and without any detrimental effect on its aesthetical properties. Protective products must preserve stones in their state of aging and prevent further decay. This generally means applying a coating to the stone surface. Consolidation, on the other hand, aims at stabilizing a friable material, while allowing weathering to take place at a natural rate as a result of natural processes.

The requirements for consolidant products mainly consist in a good stability, compatibility with the substrate [1,2], and a suitable penetration depth. A good consolidant should primarily reduce the rate of decay of the stone surface and improve its mechanical properties. In the ideal case, the treated stone should mimic sound stone in as many characteristics as possible, especially in terms of porosity, permeability, thermal expansion, water absorption and desorption, and color.

The main challenges in stone protection are related to the creation of a barrier against water penetration and the protection of the stone surface from pollutants and organic/inorganic particles deposition, while also ensuring the aesthetical compatibility with the substrate (i.e., color changes within acceptable ranges), the minimum alteration of the water vapor permeability and the reversibility of the treatment [3]. In this perspective, hydrophobic coatings [4], antifouling treatments [5] and self-cleaning nanoparticle-based protectives [6] are currently on the light of the research in stone preservation field [7].

Usually, tests based on standard recommendation procedures are applied to evaluate the efficiency of consolidants or protective products, mainly aiming at verifying their harmlessness with respect to the aspect of stones and their physical properties [8]. However, up to now, in spite of the huge literature in the field, no standard procedures and/or univocal methods for assessing the efficiency of consolidants and protective products are proposed [9]. Going beyond the classic approaches, usually using microscopy, micro-drilling, and ultrasound velocity tests [10], imaging techniques could add relevant information, as demonstrated by the recent applications in archaeological, geological, and industrial fields [11,12]. Indeed, neutron and X-ray imaging techniques allow inspecting and analyzing numerous properties and processes, such as porosity, water movement, degradation effects, amount and distribution of degradation products, or penetration depth of protective and consolidant products [13–19].

In the case of consolidants, penetration depth and bonding to the substrate are the two main aspects to investigate. Bonding ability greatly depends on both chemical composition of the product used (including solvent and concentration) and the stone surface [10]. Usually, products having a composition similar to that of the stone are preferred. However, this appears a non-exclusive requirement, such as in the case of silicate-based networks largely employed in marble and limestone consolidation [20–22].

When a new product is tested on a new substrate, the first question is related to the artificial aging of stones to mimic the weathering of in situ conditions. For limestones, salt weathering is a major cause of natural degradation. However, since salts are usually difficult to remove and could influence the consolidation test results [23], laboratory tests are also performed on unweathered stones. Another aspect regards the application method [24–26], where brushing is sometime preferred because it ensures a good product application and a relatively controlled equilibrium between penetration and solvent evaporation. Of course, the testing of a new product requires preliminary tests aiming to identify the most suitable methods and procedures [10,27].

Among the new products synthesized for conservation of cultural heritage materials, hybrid formulations have recently been proposed for inorganic [28] and organic materials [29,30]. The term hybrid refers to a product usually developed by sol-gel processes [31] and characterized by both the robustness of an inorganic skeleton and the functional properties of an organic material [32]. With regards to consolidants, the current researches have mainly explored the potential of TEOS-modified products by using organic additives with the aim to overtake the limitations of negative long-term effects of tetraethoxysilane [33–36] and to improve performances of consolidants, including water repellent properties [37]. Among hybrid formulations, silicon-based products are becoming more and more popular, due to the good processability and the stability of Si—C bonds during the formation of a silica network, which allows the production of organic-modified inorganic networks in a single step. Soft-matter chemistry applications are also focused on designing hybrid coatings having mainly the scopes to improve repellency [38,39], performances [40] and durability of protective products against aging [41].

To evaluate the possible use of these new products for cultural heritage conservation, and better understand how to tune hybrid formulations toward a better compatibility with highly porous and calcite-based stone substrates, in this study we tested a hybrid patented product (PAASi, [42]) and two commercially available hybrid products (a consolidant named AlSiX and a hydrophobic product named WS3) on a calcarenite substrate (named Sabucina Stone). The synthesis of consolidants was designed to overtake possible limitations of such products. For the PAASi product, the amine would promote interaction with limestone substrate, while for the AlSiX product, the organic chains would contribute to limit shrinkage during curing process. The compositional and physical properties of the stone selected for consolidation tests, especially its high porosity, give also the opportunity to inspect the potential use of the products on highly porous materials, often difficult to consolidate [24]. To evaluate bonding and penetration ability of the products, consolidation tests were performed on an unweathered treated substrate, to avoid the difficulties related to the artificial weathering, such as the presence of salts and no proper desalinization. Efficiency and suitability of the products were firstly evaluated by monitoring absorption, desorption, color, resistance to artificial weathering, and pore structure changes. Thus, non-invasive investigations by using X-ray and neutron sources were performed to visualize products inside stones and the possible pore network modification. Finally, additional structural information on the employed products was obtained with small angle neutron scattering (SANS) technique.

Consolidants were applied by immersion to have maximum penetration depth and fully impregnated specimens. In view of combining both consolidation and a protective application, hydrophobic coating was therefore applied by brushing on the treated specimens. Finally, for structural studies by SANS, samples were treated by both brushing and immersion, to evaluate the pos-