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# Coating's influence on water vapour permeability of porous stones typically used in cultural heritage of Mediterranean area: Experimental tests and model controlling procedure

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ABSTRACT

Water vapour flux into the porous microstructure represents a crucial factor capable of influencing the degradation of porous materials. This fact is of utmost importance especially considering materials installed in cultural heritage. The necessity to preserve stone artworks pushes to perform surface protective coatings that create an intermediate sacrificial layer between stone and the environment. High hydrophobicity and high permeability of water vapour must be one of the most important requirements of a protective film. These features depend upon the nature of coatings as well as the porous microstructures. In order to control coatings' effects and their influence on final water vapour permeability ($\delta$) properties, a new modelling procedure has been proposed. The study is conducted on a porous limestone, namely Pietra Leccese, which is being largely used for historical constructions in Mediterranean. The average experimental water vapour permeability $\delta_{exp}$ is $4.83 \times 10^{-4}$ and $3.86 \times 10^{-4}$ (g/m d Pa) respectively for untreated and treated PL stone, while the average model prediction $\delta_{IFU}$ is $4.87 \times 10^{-4}$ and $3.77 \times 10^{-4}$ (g/m d Pa) respectively for untreated and treated PL stone. The good agreement between experimental and calculated data shows that the proposed modelling procedure could represent a good tool for designing and controlling protection activity on cultural heritage.

## 1. Introduction

In the past, the stone has always been considered strong and everlasting, capable of lasting for thousands of years. Just two centuries ago, it was realised that the stone is also sensitive to degradation and is required to be properly preserved. Consequentially, the necessity of new instructions, institutional regulations and the restoring professional figure was raised up. Conventionally, degradation processes are divided into three forms; chemical, physical and biological weathering. But in reality, this schematisation is not possible. Several degradation factors act synergistically causing the same effects. Owing to this reason, conservation does not imply a single approach, rather there are several techniques and methods proposed to achieve the aim of preserving cultural heritages. In particular, a widespread way to protect monumental artworks is the use of surface protective coatings that create an intermediate sacrificial layer between stone and the environment. Traditionally, inorganic protective coatings were widely used due to their mineral component, which guarantees the physical and chemical affinity with the stone. The most used stones were calcium or barium hydroxides based, sodium or potassium aluminates based and potassium or fluorine silicates based compounds. On the one hand, they are preferred for their compatibility with the substrate and re-treatability thanks to the structural and chemical similarity with stone materials. On the other hand, they possess some drawbacks; an intrinsic fragility and low mechanical properties. Organic protective coatings originated in the past, when beeswax, vegetable oils and natural resins were used and the commercialisation of synthetic polymeric products started in the XX century. Organic products characterised by high molecular weight can be applied to solvent solutions, water based emulsions or pure state (monomers or oligomers). In the following years, several acrylic and methacrylic, silane/siloxane, fluorinates' compound coatings were widely employed in the restoration fields [1–5]. High hydrophobicity and high permeability of water vapour are the most important requirements of a protective film. In

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fact, the capability to hinder the liquid water penetration, the major causes of degradation trigger and not inhibiting the natural breathability of the stone are the most significant requisites for a protective coating. Unfortunately, many products commercially available and widely used so far have this great disadvantage. For instance, perfluoropolyethers are often employed due to their evident hydrophobic capability, strong chemical inertness and high resistance to thermal-oxidation. Thanks to low viscosity, they are able to guarantee good penetration into the stone pores, but this feature also represents a great limitation because of their migration inside the stone porosity with the passage of time. Consequentially, a loss of protection effectiveness and a low permeability to water vapour are assessed [6].

Nanotechnology has been providing desirable concepts and materials for the conservation of the cultural heritage. For instance, in recent years, different scientists have proposed the application of sub-micrometric inorganic particles for the protection and/or consolidation of stone materials [6–11]. However, most nanocomposite systems, developed in the last ten years, presented some disadvantages in terms of permeability. As an example, layered polymeric nanocomposite systems, composed of organic polymers and organomodified silicate as inorganic nanometric layered reinforcements showed great interfacial area per volume between the nanosheets and the polymer that assured higher chemical, thermal and mechanical resistance with respect to the unmodified resin. On the other hand, a low gas and vapour permeability at low volume fraction of inorganic phase was evident [11]. For all these reasons, the study and the development of innovative systems capable of overcoming the limitations of the traditional organic protective products is nowadays the objective of research of many scientists.

Recently, the authors proposed several experimental organic and nano-stuctured organic-inorganic products for the protection of stone elements aimed at overcoming the deficiencies associated to the chemical composition of acrylic based coatings as well as the curing method, through the use of alternative high energy radiation and the low permeability of water vapour of such commercial or experimental products [12–15].

Conservation design must take into account the microstructure of the materials that have to be treated [16]. Indeed, the protection effect is related to the original porous microstructure. Usually, in order to obtain specific information regarding mass transfer variation after treatments, experimental tests with statistical validity are performed using stones from quarries, which are similar to those actually used in the studied cultural heritage. This fact is owing to the necessity to preserve, as much as possible, the original state of the historical monumental artworks. However, the similar materials used for experimental activity could have remarkable differences owing to macro- micro-climatic exposures, which condition weathering process kinetics [16].

Although, the possibility to withdraw significant large dimension samples is excluded, but it is possible to remove small and irregular fragments, which have a typical volume approximately equal to 1 $\mathrm{cm}^3$ [17]. These samples, which are not suitable for classical and direct experimental tests for obtaining water vapour permeability values, can be used, instead, to perform mercury intrusion porosimetry (MIP) inspections. MIP results consist of pore cumulative curves of mercury intrusion, which allow knowing pore volume fraction and pore size distributions of porous materials [17].

For these reasons, the possibility to indirectly develop methods capable of obtaining fluid transfer properties based on MIP curves would be highly useful. Modelling procedure having these characteristics must be able to describe microstructures in terms of geometric parameters without empirical terms. This task appears immediately hard especially because the systems are naturally irregular, fragmented and apparently chaotic for being reproduced by *Euclidean* geometry. Concerning this complexity, the development of a new geometry capable of simulating morphological shapes observed in nature is a key to understand physical phenomena regarding porous materials. Recently, this role is covered by Fractal Geometry, which was formalised by Mandelbrot in 1970s [18]. The figures elaborating fractal geometry concepts are called *fractals* and this term is derived from Latin word “*fractus*”, which means “broken”, “indented”, “irregular”, etc. The principle characteristic of fractal figures is represented by the fact that the dimension could be non-integer. The practice example is a sheet of paper, which can be assimilated to a surface with Euclidean dimension equal to 2. In case of rolling this sheet of paper into a ball, the Euclidean dimension is not 2, but is not even 3, because it is not a volume. Fractal geometry defines this dimension as a non-integer value between 2 and 3. In the same way, Fractal geometry is able to describe clouds, mountains and surfaces, which are not ascribable to spheres, cones or geometric planes respectively. Moreover, fractals are constructed by a self-similarity iteration process. Indeed, the degree of their irregularity is identical at all scales of observation [18,19]. This property is very important for generating figures that can be assimilated to porous microstructures, in particular for those having different pore size classes.

For these reasons, Fractal geometry has been used to explain different characteristics behaviour of porous materials. Liu et al. [20] proposed fractal length distribution fractal model in order to theoretically study fluid flow in fractured rock masses. Miao et al. [21] studied rocks with shear fractures and formalised a model to predict permeability as a function of their fractal dimensions. The results show that permeability values increase with the increase in pore volume fraction and the density of fractures. Moreover, they compared their model data with numerical simulation available in literature. Cai et al. proposed a fractal model of spontaneous imbibition based on Hagen-Poiseuille flow. The proposed modelling approach, taking into account different sizes, shapes and tortuosity of the pores and the initial wetting-phase saturation, is capable of describing the imbibition process in several porous media; natural or artificial [22–25]. Particularly, relevant process results into the application of fractal geometry in order to develop the imbibition time exponent of classical Lucas–Washburn (LW) equation. Here, the time exponent is theoretically related to the tortuosity fractal dimension in LW-Cai-Yu fractal model [23].

Recently, a new fractal approach has been proposed for predicting several properties of porous materials; permeability, sorptivity, mechanical properties and heat transfer [26–29]. It is based on mixing together different fractal base units and non-porous parts in order to reproduce pore microstructures as pore volume fraction and pore size distribution of fractal or non-fractal materials.

In this work, for the first time, in order to formalise an important tool for controlling weathering process and for conservation design, an IFU model has been applied to reproduce water vapour permeability kinetic of porous stones, as received and treated, usually installed in cultural heritage. The complete agreement with experimental data confirms that IFU is a promising non-invasive approach for preliminary inspection on historical artworks.

## 2. Materials and methods

### 2.1. Stone material: PietraLeccese (PL)

*PietraLeccese* (PL) is a fine-grained limestone, characterised by a white-yellow colour, classifiable as wackestone. It is composed of fossil fragments (shells and algae) and numerous little grains of glauconite and phosphatic nodules. The size of bioclasts is around 150 μm and the micritic matrix is composed of clay minerals [30].