The protection of natural stones in outdoor environment: new perspective to a difficult challenge

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The issue of conservation of the architectural heritage is strongly related to climatic conditions and air pollution.

Information on both the air quality and microclimate are needed to effectively evaluate cultural heritage conservation methods.
Interaction Material / Environment

Architectural Heritage durability

Material
- Chemical properties
- Physical properties
- Mechanical properties
- Mineralogical properties
- Micro-structure

Environment
- Climate Region
- Micro-climatic conditions
- Air quality & pollution

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Heritage conservation? What does it mean in Europe?
The process of degradation is the adaptation of stone materials to the **prevailing environmental condition**.

The process of degradation occurs at the very surface of the building, that is the **interface material/environment**.

Since XXth cent. the kinetic of the process has been dramatically speeded up according to the **increase of atmospheric pollution**.
The determinant factor: microstructure and porosity

Carrara marble

Candoglia marble
High value Architectural Heritage
Milan, the Cathedral

1961

2000

10,500 m² of marble
12 spires
500 sculptures
25 large low-relieves
Conservation work of the facade 2003-2009
4 dramatically important keywords:

1. **Multi-disciplinarity** well structured working team, architects, material scientists, geologists, specialized companies

2. **Knowledge** of materials, treatments and their long term behavior, experience

3. **Compatibility** new approach to consolidation and protection

4. **Reversibility / Retraetability**

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**Project guidelines**
Going towards a sustainable conservation policy: what kind of treatment?

1. Cleaning
2. Surface Consolidation
3. Adhesion and Sealing
4. Surface Protection

“There is hardly a polymer which has not been suggested and used for a conservation application” C.V. Horie 1990

Phases of the maintenance and conservation work
What is «surface protection»?

Direct surface protection is the application of materials with specific properties to stone surface in order to protect it towards deterioration agents, such as water, water vapour, marine spray, gas pollutants, dust, particulate matter, vandalism etc.

- Water-repellent treatments
- Anti-graffiti
- Antifouling treatments

Main classes
Protective treatments: requirements

1. **Good water repellency**
2. Maintain **water vapor permeability**
3. Good **adhesion** to the substrate
4. Negligible **color alteration**
5. Chemical **inertness**
6. Long term **durability**
7. **Reversibility** (solubility)
### Alkyl silicon polymers

It includes different products: alkyl siliconates, alkyl silanes, siloxanes, polysiloxanes. They are the most used due to their higher durability and stability.

### Fluorinated and partially fluorinated polymers

Perfluoropolyethers, fluorinated elastomers or acrylics, improved water repellency and resistance to photooxidation. Rather poor ability to stick to the stone.

### Acrylcs

Poor performances in terms of durability and aesthetical compatibility (rapid loss of water repellency on weathering), Paraloid B72, acrylic co-polymers.

### Low MW, Inorganics

They include low molecular weight inorganic compounds, ammonium oxalate promote the formation of calcium oxalate which is more stable than calcite to acid rain.
Main two types of unique properties of nanostructures:
1) **novel optical properties** due to quantum confinement effects;
2) **changes in reactivity and mechanical properties** due to the small physical dimensions and large surface area.

The application of **nanoparticles** and **nanocomposites** in the field of conservation lead to significant improvements:

1. high **physico-chemical compatibility** with the constituents of works of art;
2. either non-toxic or they exhibit a significantly **reduced toxicity**;
3. their use allows **greater control** of the restoration intervention

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Baglioni et al. *Nanotechnologies in the Conservation of Cultural Heritage: A compendium of materials and techniques*
Why nanostructured protective treatments?

Water repellency
Water absorption
De-polluting activity
Anti-fouling
No color alteration
Adhesion & reversibility
Durability

Challenges in Stone protection

Nanomaterials:
1. Enhanced protection efficacy
2. Additional properties (photocatalytic, antifouling, antibacterial)


Innovative protective treatments

Enhanced water repellency
Self-cleaning & de-polluting:
Anti-fouling property

- **Degradation of pollutants** (inorganic and organic) that can be washed away by rain
- **Preventive strategy** towards stone degradation and biocolonization (favoured by water absorption)
- **Reduction of maintenance** and **costs** due to reduction of persistent deposit
Innovative protectives: nanocomposites

- The introduction of nanoparticles in polymeric media enhance their protection effectiveness
- Higher static contact angle: superhydrophobic coatings

A. Sierra-Fernandez et al. MATERIALES DE CONSTRUCCIÓN, 2017
Nano-TiO$_2$ is able to degrade organic and inorganic pollutants.

It is able to make the surface superhydrophilic, easily removing dust by rainfall.

A. Sierra-Fernandez et al. MATERIALES DE CONSTRUCCIÓN, 2017
Oslo Opera House - Carrara marble tiles
Laboratory testing for the selection of protection treatments

In collaboration with:
- Technical University of Crete
- NanoPhos

- nanoTiO2 alkylalkoxy silane
- Reference water repellent polysiloxane
- Calcium oxalate/silica nanocomposite
- Reference Ammonium Oxalate

Evaluation of application methodology, solvents, amount

- By brush
- By capillary absorption
1. **SurfaPore FX SB_SPA** (NanoPhos): solvent based calcium oxalate-silica nanocomposite  
2. **SurfaPore FX WB_SWP** (NanoPhos): water based calcium oxalate-silica nanocomposite  
3. **Silres BS 290_BS** (Wacker): alkylsiloxanes (8 wt.% in white spirits)  
4. **PF4_PF** (ChemSpec) nano-TiO₂ alkylalkoxy-silane nanocomposite  
5. **Ammonium oxalate_AO** (Bresciani) (5 wt.% in water)

<table>
<thead>
<tr>
<th>Product</th>
<th>Amount applied treatm. (mg/cm²)</th>
<th>ST.dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPA</td>
<td>0,49</td>
<td>0,08</td>
</tr>
<tr>
<td>SPW</td>
<td>1,84</td>
<td>1,40</td>
</tr>
<tr>
<td>BS</td>
<td>0,52</td>
<td>0,42</td>
</tr>
<tr>
<td>PF</td>
<td>2,54</td>
<td>0,08</td>
</tr>
<tr>
<td>AO</td>
<td>3,73</td>
<td>0,10</td>
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</table>
Characterization of the different products: **molecular** (FTIR spectroscopy) and **morphological characterization** (TEM and SEM-EDX)

Evaluation of **compatibility and effectiveness** and harmfulness of the treatments applied to the marble specimens:

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Standards</th>
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<tbody>
<tr>
<td>Water absorption by capillarity</td>
<td>EN 15801</td>
</tr>
<tr>
<td>Water vapour <strong>permeability</strong></td>
<td>EN 15803</td>
</tr>
<tr>
<td>Static contact <strong>angle</strong></td>
<td>EN 15802</td>
</tr>
<tr>
<td>Surface <strong>colour</strong> monitoring</td>
<td>EN 15886</td>
</tr>
<tr>
<td>Treatment <strong>morphology</strong> and penetration depth: SEM/EDX</td>
<td>Non-st</td>
</tr>
<tr>
<td><strong>Distribution</strong> of nano-particles: SEM/EDX and TEM, AFM</td>
<td>Non-st</td>
</tr>
</tbody>
</table>
Surface morphology after treatment: comparison among the different products observed by ESEM, 2000X

Untreated
SPA
SPW
BS
PF
AO

Lucia Toniolo, Full Professor Dept. CMCI

POLITECNICO MILANO 1863
- Increase of the water contact angle for SPA, BS and PF
- Reduction of the water contact angle for SPW and AO
Reduction of the water absorption after the application of the treatments especially for BS, SPW and SPA
- Reduction of water vapour permeability for SPA, SPW, BS (high reduction) and PF
- Increase in the water vapour permeability in sample treated with AO
The selected products show different properties and performances according to their chemical nature and microstructural characteristics.

All treatments are compatible preserving the aesthetic properties since the surface color change (ΔE*) is lower than 3, but it is necessary a control after ageing in outdoor environment.

Given the function and the position of the Carrara marble tiles (pavement in outdoor marine exposition) it will not be so appropriate to drastically improve the water repellent character of the stone and reduce water vapour permeability.

At the present stage of the research the suggestion is to promote a pilot application onsite of the Surfapore solvent based nanocomposite (SPA), which could grant a good protection and stabilize the calcite grains of the marble, thanks to the presence of nano-CaOx. The comparison with a traditional treatment like BS is always recommended.
At the same time, the materials developed in the framework of the H2020 NanoCathedral project could be surely useful and constitute a valid alternative and a very important experience for the set-up of the maintenance procedure of the Oslo Opera House building.

Thank you for your attention
I would like to thank greatly the colleagues, coworkers and students of the Laboratory Materials and Methods for Cultural Heritage.

Please visit the website http://midar.chem.polimi.it

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