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SCIENCE and ART: A Future for Stone

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Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

EUROPEAN PROJECT
"NANO-CATHEDRAL: NANOMATERIALS FOR CONSERVATION OF EUROPEAN ARCHITECTURAL HERITAGE DEVELOPED BY RESEARCH ON CHARACTERISTIC LITHOTYPES"

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Abstract

Europe has significant cultural and environmental diversity together with an exceptional ancient architecture and built environment. From the point of view of conservation, this architectural excellence and heritage may present degradation problems related to the variety of stone materials used for their construction. In the present project five different medieval cathedrals and a contemporary opera theatre were selected as they may be considered as representative of both different environmental conditions and types of stones (limestones, sandstones and marbles) in Western Europe. The project aims at developing new materials, technologies and procedures for the restoration and conservation of stone in ancient cathedrals and monumental buildings, with a particular emphasis on the preservation of the originality of the building materials and on the development of tailor-made approach to tackle the specific problems. The original materials will be analysed and classified, evaluating their connection with historical exploitation of quarries as a source of building materials. Nanomaterials suitable for the consolidation and protection of stones will be developed aiming at providing the best technological answer for the preservation of different types of stones, according to porosity and mineralogical and chemical features. The exploitation of the project will bring about the adoption of best practices for the preservation of the cathedrals and high quality buildings by selecting the most advanced nanotechnologies.

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1. Introduction

1.1. Project "Nano-cathedral"

In the framework of the EC Horizon 2020 Nano-Cathedral project[1] launched in 2015, nanomaterials for the preservation of stone based monuments have been designed as a result of a collaborative effort of European research Centers, companies involved in the development and production of engineered inorganic nanoparticles, Conservation Institutions and Foundations managing monumental buildings. The general objective of the three-year project is the design, production and evaluation of different types of inorganic and polymeric nanoparticles as well as nanoparticles based formulations, to be applied as protective and/or consolidation treatments onto different lithotypes on European monuments characterized by a variety of environmental exposure conditions. In particular, the Cathedral of Pisa (Italy) and the Cathedral of Santa María of Vitoria-Gasteiz (Spain) are representative of south European "Mediterranean" climate in coastal and continental regions, respectively; the Sint-Baafs Cathedral of Ghent (Belgium), the Cathedral of St. Peter and Mary of Cologne (Germany) and the St. Stephen's Cathedral (Vienna), are included as representative of a Central-North European climate in continental regions. Moreover, the Oslo Opera House (Norway) was considered as an example of a contemporary building cladded with white Carrara marble. The stones used for the construction of the buildings have been analysed and classified, evaluating their connection with historical exploitation of quarries as a source of building materials, thus improving the knowledge of the architectural and artistic heritage and the connections with the regional context. For this purpose a general protocol has been defined for the identification of the petrographic and mineralogical features of the stone materials, the evaluation of their state of conservation, the identification of correlations among the relevant state of decay, the material properties and the local macro and microclimatic exposure. The innovative nanomaterials, that will be developed, will be applied on stone materials taken from quarries representative of the selected lithotypes, and they will be tested before and after application of the consolidation and/or protection products to evaluate the effectiveness of the treatments, following a protocol of laboratory tests which include microscopic observations, colorimetry and spectroscopic analyses. Finally, the best formulations of consolidants and protective treatments will be applied on pilot-areas selected in each building and non-destructive tests will be carried out to monitor their effectiveness and durability.

1.2. Nanomaterials for stone conservation

Since '80s, the scientific research has been devoted to the development of nanomaterials to be applied in a wide range of fields, including the conservation of Architectural Heritage. Compared to traditional materials and methods, the innovative nanomaterials show enhanced effectiveness in their main properties as their higher surface area make them more reactive. Regarding the class of stone consolidants, one of the first synthesized

[1] H2020 Grant Agreement N.646178; NMP-2014-2015/H2020-NMP-2014-two-stage

nanomaterial is nanolime, that is a water or alcoholic dispersion of $Ca(OH)_2$ nanoparticles. Nanolime has been used for the consolidation of calcareous stone and wall paintings, since it presents different advantages compared to traditional limewater: higher reactivity, deeper penetration in the substrate, reduction of carbonation time and higher stability (Chelazzi *et al.* 2013, Rodriguez-Navarro *et al.* 2013). Different commercial nanolime and dispersions of nano-SiO_2 are available on the market and their use is becoming more common among restorers, despite nowadays the most used consolidants are alkoxy-silane and oligomers. In order to overcome the drawback of alkoxy-silanes related to the formation of cracks of the silica gel, particle-modified consolidants, based on the introduction of different nanoparticles in pre-polymerized tetraethoxysilane, have been proposed (Miliani *et al.* 2007, Kim *et al.* 2009). Another interesting nano-consolidant is the one proposed by Verganelaki, which consists in the incorporation of nanoparticles of amorphous calcium oxalate monohydrate in TEOS to form a crack-free nanocomposite, with a good penetration depth inside the substrate, able to increase the strengthening properties of calcareous building stones and cement mortars (Verganelaki *et al.* 2015). Nanotechnology is also applied for the synthesis of protective treatments for stone materials, realized by adding different nanoparticles (SiO_2, SnO_2, Al_2O_3) inside polymeric media (poly(methyl methacrylate), functionalized perfluorinated polyether and polyalkylsiloxane) to increase the stone surface roughness (Manoudis *et al.* 2009, Facio and Mosquera 2013). These nanocomposites are able to confer super-hydrophobic (water contact angle > 150°) and self-cleaning properties to the stone. Moreover, TiO_2 nanoparticles have been used for the synthesis of self-cleaning consolidants and protective treatments because of their photocatalytic property to promote the degradation of inorganic and organic pollutants and their ability to create superhydrophilic surfaces (Munafò *et al.* 2015). Among TiO_2-based self-cleaning coatings for Cultural Heritage stone surfaces, two different categories can be identified. The first one includes hydrophilic nano-TiO_2 dispersions (Quagliarini *et al.* 2013), whereas the second one comprises hydrophobic and superhydrophobic nanocomposites (Kapridaki *et al.* 2014).

The results of the current and more recent literature demonstrates the potential of nanostructured consolidants and protective treatments for the conservation of architectural heritage, since they can overcome the open challenges related to durability, adhesion on the substrates, effectiveness and transparency issues.

2. Survey on commercial and research stone consolidants and protective coatings

One of the activities of the Project concerns the realization of a survey to setup a database of the most applied commercial products and the most relevant research products from the current scientific literature in Europe for the consolidation and the protection of natural decayed stones. The collected data are coming from the Project Partners on the basis of their professional and research experience and the elaborated data are strictly connected to this provenance; therefore, the database is not an exhaustive collection of all the commercial or research products available. Among commercial products, the total number of different consolidant materials is 37. They can be divided in three main chemical classes: alkoxy-silane and oligomers, acrylics and low molecular weight inorganics. 12 of them contain nanoparticles in the formulation, in particular $Ca(OH)_2$, SiO_2, ZrO_2, Al_2O_3 (Fig. 1). Regarding the dispersing media, the most used ones are organic solvents. Among commercial products, the total number of different protective coatings is 21, 2 of which have antifouling properties. They can be divided in 5 chemical classes: alkyl-alkoxy-silane oligomers, alkyl-aryl-polysiloxanes, fluorinated or partially fluorinated polymers, low molecular weight inorganics and vegetable polysaccharides. Among them 5 contain nanoparticles in the formulation, in particular Ag, SiO_2, TiO_2, ZnO nanoparticles (Fig. 1). Organic solvents are the most used in the formulations.

Among research products the total number of consolidants is 39, 2 of which have also antifouling properties. They can be divided in 4 main chemical classes: alkoxy-silane and oligomers, acrylics, low molecular weight inorganics and products of biomineralization. A wide range of nanoparticles have been used in the formulation but nano-SiO_2 is the most used one. Organic solvents are the most used in the formulations, which have been applied on different stone substrates, following different application methods. The total number of protective coatings is 27, 4 of which show antifouling properties and 2 of which show both properties. They can be divided in 4 main chemical classes: alkyl-alkoxy-silane oligomers, alkyl-aril-polysiloxanes, acrylic polymers, fluorinated or partially fluorinated polymers, oxalates, low molecular weight inorganics and aliphatic polyesters. Also for research protective coatings, a wide range of nanoparticles have been used in the formulation among which nano-TiO_2 is the most used one. Organic solvents are the most used in the formulations, which have been applied on different stone substrates, following different application methods.

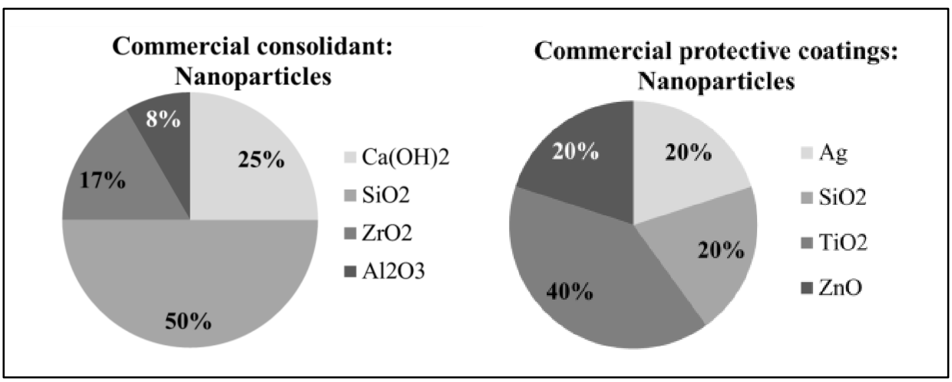

Fig. 1: Nanoparticles present in commercial consolidants (left) and protective coatings (right).

3. Selection of lithotypes

For each cathedral one lithotype has been selected (except for Cathedral of Cologne, for which two lithotypes have been selected) taking into account its petrographic properties and its representability for the building but also with respect to the European context, to grant a large scale application of the project results. The selected lithotypes are summarized in Tab. 1.

Tab. 1: Selected lithotypes for the full characterization and application of consolidation and protection formulations.

Building	Stone name	Lithotype
Cathedral of Vitoria-Gasteiz	Ajarte	Fossil limestone
Cathedral of Ghent	Balegem	Sandy limestone
Cathedral of Cologne	Obernkirchen	Sandstone
	Schlaitdorf	Sandstone
Cathedral of Vienna	St. Margarethen	Calcareous arenite
Cathedral of Pisa and Oslo Opera House	Carrara marble	Marble

4. Innovative consolidants and protective coatings

4.1. Aqueous Nanocalcite dispersions as consolidant

Nanoparticles of calcium carbonate are produced by a novel process involving colloidal particle stabilisation with either citrate or a block copolymer of poly(ethylene oxide) with poly(citrate). The optimisation of the synthetic procedure for the aqueous nanoparticle dispersions is targeting the smallest achievable particle size, since these nanocarbonates (calcite, vaterite which is a polymorph of calcium carbonate) are expected to penetrate to some extent into the porous network of degraded calcareous stones. The citrate anion plays a key role both as a nanoparticle stabiliser (it adsorbs efficiently onto the surface) and as a promoter of adhesion of the nanoparticle onto the calcareous stone surface (or inner pore surface) thanks to its ability to "chelate" the Ca^{2+} ion. Combinations of the obtained nanocalcite with conventional silane consolidants (e.g. based on TEOS) will also be explored, as it is expected that a "nanoparticle-modified consolidant" may improve the performance of simple TEOS-based treatments in terms of achieved stone cohesive strength and lower long-term damage (e.g. by shrinkage-induced micro-cracks in the silica-like material resulting from TEOS-based consolidation).

4.2. Water-borne polymeric and hybrid polymer/inorganic nanoparticle formulations

New self-stabilized amphiphilic or hydrophobic copolymers are being synthesized, as components of either consolidant or protective formulations, respectively. In particular, the composition and structure of the (acrylic) copolymers are designed to provide one or more of the following features:

i) Enhanced stability to photo-oxidative aging, by inclusion of comonomer units bearing the 2,2,5,5-tetramethylpiperidine (or Hindered Amine Light Stabilizer, HALS) group in the side chain;
ii) A combination of acrylic and methacrylic comonomers (e.g. methyl methacrylate, butyl acrylate) in a mole ratio providing the required balance of thermal and mechanical properties, while keeping the polymer photooxidative sensitivity at a minimum;
iii) Side-chain semifluorinated comonomers for enhanced hydrophobicity and chemical stability;

iv) One terminal hydrophilic short "block" of either poly(acrylic acid) (PAA) or poly(ethylene oxide) (PEO) to provide the polymer particle with the required colloidal and storage stability, without the addition of low molecular weight surfactants.

Depending on the expected performance and material requirements, the aqueous colloidal dispersions are synthesised according to one of the following two methods:

a) Conventional free radical emulsion polymerisation, yielding a high molecular weight random copolymer with uncontrolled comonomer distribution and requiring addition of a molecular surfactant for colloidal stabilisation during and after synthesis;
b) The so-called "ab initio" controlled RAFT (Reversible Addition Fragmentation Transfer) polymerisation, which may be performed in "soapless" conditions (without added surfactant) and leads to the formation of amphiphilic block copolymers, self-assembling into polymer nanoparticles of controlled size (typically within the 50-150 nm range). In this case the presence of a hydrophilic PAA or PEO block is mandatory, and may contrast the hydrophobic contribution of the remaining polymer structure. However, the PAA block may contribute to "anchoring" the polymer either to the stone surface, thus providing consolidation effectiveness, or to inorganic nanoparticle surface in hybrid formulations used as protectives. An advantage of the PEO block, on the other hand, is its inertness towards carbonatic stones and its photodegradation behaviour leading to fragmentation and eventually self-removal of this hydrophilic component from the polymer layer.

The specific contributions of these structural features to the ultimate polymer properties are assessed by a broad range of analytical techniques to fully characterize the relevant structural (by spectroscopies), morphological (by Dynamic Light Scattering and electron microscopy) and film surface (by contact angle, Zeta potential, and ATR-FTIR analyses) features.

5. Conclusions

The main objectives of this Project are: innovation in materials technology and rationalization of the conservation policy, affording a renewed knowledge of the complex system - treatment/stone substrate and of the durability threshold of these treatments.

The wide experience and literature on the nanostructured materials in the field, the multidisciplinary approach and the inclusion of industrial partners – Colorobbia Consulting Srl, Chem-Spec srl, Tecnologia Navarra de nanoproductos sl – will grant the possibility to set-up new affordable conservation treatments.

In the first semester of the Project, a decisive state of the art about the use of nanotechnologies for the consolidation of stone materials was carried out, assessing nano-SiO_2 and nanolime as the most used nanostructured materials. In the field of protection and water-repellent treatments for stone surfaces, TiO_2 and ZnO nanoparticles are the most employed in dispersions or formulations.

In the framework of this Project, some different new nanomaterials have been already designed and prepared. An important achievement is the set-up of the new synthetic procedure for nanocalcite which will be used and tested as simple dispersion, which can easily penetrate the porosity of calcareous stone materials, or will be used as an additive in particle modified consolidants (i.e. modified TEOS) and improve the adhesion of the system to the crystalline substrate. New self-stabilized amphiphilic or hydrophobic copolymers have been already synthesized to be used as protective treatments or in hybrid system covering nanoparticles of different nature.

A short testing protocol will be carried out in the following months to assess the most promising nanomaterials. Actually, the Technology Readiness Level of the project should be at least 5, as the developed technologies will be validated in lab and *in situ,* that is on the selected monuments.

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