

**NANOMATERIALS FOR CONSERVATION / PRESERVATION OF  
CULTURAL HERITAGE**

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In the last years the issue of conservation and preservation of cultural heritage has gained high interest both in scientific research and in the restoration of various monuments from universal heritage. The aim of this paper is the presentation of hydroxyapatite as a non-toxic and environmentally friendly nanomaterial that could be involved in the conservation of heritage monuments (chalk, marble or travertine), and the results obtained after applying it on these surfaces. Some scientific analytical investigations are used to detect the changes in the structure and colour of the surfaces where it had been applied. These nanostructured products for cultural heritage preservation highlight increased performances without changing the substrate color.

Keywords: hydroxyapatite, analytical investigations, nanomaterials.

## **INTRODUCTION**

The study of architectural surfaces and materials used in restoration joined an increased interest in the last decades, in good connection with reviving some buildings with environmental and aesthetic decorative elements, and obeying art history and architecture elements, too. In such context, it is important to allow the interaction between the substrate and decoration, evaluation of the degradation processes, mostly physical, short or long term, physical and chemical changes of materials while restored and products for restoration, architectural surfaces and forms of biodegradation process (Clarke and Ashurst, 1972; De Witte *et al.*, 1985).

The sculptures and constructions made of marble, travertine and limestone have a special position among the unique architecture ensemble from many locations.

Limestone is a sedimentary rock composed mostly of calcite and aragonite, as different crystal forms of calcium carbonate. Travertine belongs to the limestone family also known as calcium carbonate. It is formed by minerals dissolving in ground water and then deposited on the earth's surface by rivers, natural springs, or geysers. The major disadvantage of travertine is that it is brittle and susceptible to cracking, and sensitive to the freeze and thaw cycle. Marble is also a type of limestone that has had additional heat and pressure applied to it by the earth's crust. Chalk is a soft, white, powdery limestone consisting mainly of fossil shells of foraminifers. External factors such as rain, snow, temperature, wind and atmospheric pollutants, could induce the weathering of all these stones. Rainwater and temperature can lead to deterioration, as well as the salt migration within the stone.

Nanomaterials exhibit excellent chemical-physical features for application in the conservation science of art works, being able to slow down the degradation processes of artifacts, by comparison with traditional methods, widely described in literature (Ion *et al.*, 2015a). The aim of this paper is to test some nano-consolidants based on hydroxyapatite, for consolidating the travertine, marble and limestone chalk stone, used

as models for architectural monuments. Hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , has the advantage of similar crystal structure and close lattice match to calcite (Ion *et al.*, 2015b). The composition, the changes in the structure in time of the surfaces and color changes will be reported by using some analytical techniques: optical electron microscopy, Fourier transformed infrared spectroscopy (FTIR), colorimetry and Raman spectrophotometry tests.

## **MATERIALS**

### **Specimens Samples Preparation and Consolidants**

Different samples were prepared, such as travertine, marble and limestone chalk (40 mm × 40 mm × 40 mm) in order to achieve to distinguish the difference between non-treated samples and to observe the influence of consolidant used during the treatment. After the drying process the substrates were left to cool for two hours in a desiccator and their appearance was examined. Hydroxyapatite was used as consolidant, obtained in the lab by chemical precipitation method from calcium nitrate tetrahydrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and dibasic ammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$ , at room temperature. The powder was dry mortar in a mortar and pestle and then calcined in alumina crucible at 1200°C for 1h. The application of the consolidant was carried out by brushing. Dispersions have acquired a white opalescent appearance with uniform size of 30 nm.

### **Characterization Techniques**

The following techniques were used: Fourier transformed infrared spectroscopy (FT-IR, Perkin–Elmer Spectrum One FT-IR Spectrometer), using the KBr pellets method, Dynamic Light Scattering (DLS) technique, for particles size and their size distribution, Stereozoom microscopy achieved with a binocular Optika microscope (100x – 4000x), for morphology evaluation of the analyzed stones.

Color measurements, achieved with a spectrophotometer (Carl Zeiss Jena M40) under a D65 light source and an observer angle of 100. The CIELAB color parameters clarity ( $L^*$ ), red/green colour component ( $a^*$ ) and yellow/blue colour component ( $b^*$ ) and their derived magnitudes: chroma ( $C^*$ ) and tone ( $H^*$ ). The total color differences  $E^*$  were calculated using specific formulas (JIS, 2009).

## **RESULTS AND DISCUSSION**

Stone materials of mineral-inorganic nature, due to their hydrophilic properties, need special treatments for their conservation. Stone can be deteriorated by acid attack (caused by rains and humidity condense in polluted urban atmospheres which induces corrosion to carbonatic materials such as calcium and/or magnesium carbonate based stones while silicatic stones are only poorly affected) and by soluble salts cyclic crystallization (Ferreira Pinto and Rodrigues, 2008). Some studies on environmental influences on degradation stone monuments, considering factors such as temperature (average, minimum, maximum), number of days of frost and sunny days, humidity annual average rainfall amount and chemical composition, air currents, will be evaluated, too, knowing that carbonates have been detected as the predominant in the body of the church with sulphates impurities (Price, 1996).

Stone consolidating materials as inorganic materials should produce insoluble phase within the voids and pores of a stone. The results show that some properties of conservation materials can be improved with the presence of nanomaterials (Mosquera, 2008). This should favor nucleation of HAp on calcite, and might permit formation of a coherent layer of HAp on the surface of marble.

Travertine is a form of limestone with a fibrous or concentric appearance formed by a process of rapid precipitation of calcium carbonate (Pentecost, 2005). Travertine is a porous limestone rock (composed of calcite, aragonite and calcite weak magnesium), which has a yellowish to brown. Travertine exists in two varieties: compact travertine, which is dense and thick stratified banks (20-40 m) and layered thin laminae, white or brown. In general, travertine is porous. If the pores are closed with cement dust by grinding and polishing travertine end a surface as smooth as marble.

Marble is a metamorphic rock that may be foliated or non-foliated, composed of recrystallized carbonate minerals, most commonly calcite or dolomite (Kearey, 2001). HAp has a much lower solubility and dissolution rate having the ability to confer protection in acidic environments, with a dense coating of only about 10  $\mu\text{m}$ . The performance of HAp has already been proven in restoring the strength of weathered limestone (Sassoni *et al.*, 2011). Other workers have also investigated the use of HAp as a consolidant for marble (Yang *et al.*, 2011; Liu *et al.*, 2011; Matteini *et al.*, 2011). In this paper, we discuss its use as a surface-protective layer for chalk in order to obtain a noticeable retardation of the weathering. Chalk is a soft, white, porous sedimentary carbonate rock, a form of limestone composed of the mineral calcite. The infrared spectra, Figure 1, put into evidence different inorganic phases, as follows ( $\text{CaCO}_3$ , peaked at 1962, 1409, 715 and 603  $\text{cm}^{-1}$ ; gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), centered at 667  $\text{cm}^{-1}$ , clay minerals recognized, through the peaks from 975  $\text{cm}^{-1}$  (Si–O–Si bond) from clay, and of calcite (1018  $\text{cm}^{-1}$ ) (Derrick, 1999).

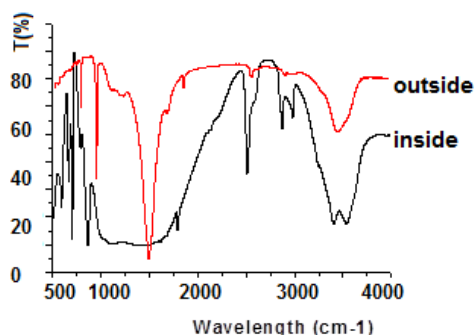


Figure 1. FTIR spectra of limestone from inside and outside building

Also, by analysing the interior and exterior limestone, the influence of the atmospheric pollutants on the limestone is visible by Raman spectra of HAp on limestone surface: it is visible the interaction between  $\text{CaCO}_3$ , peaked at 715 and 603  $\text{cm}^{-1}$ ; gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), centered at 690  $\text{cm}^{-1}$ , clay minerals from 975  $\text{cm}^{-1}$  (Si–O–Si bond) from clay, and of calcite (1100  $\text{cm}^{-1}$ ), Figure 2. Optical electron microscopy research was performed to investigate microstructure characteristic of the specimens.

Special attention was paid to the effectiveness of consolidation treatment observable namely in the pores and cracks. It is mostly the size of pore openings and the chemical/mineralogical nature of the pore walls which are of relevance to the treatment by consolidant, Figure 3. Travertine treated with HAp, could be considered as effective in preserving stone material, Figure 4.

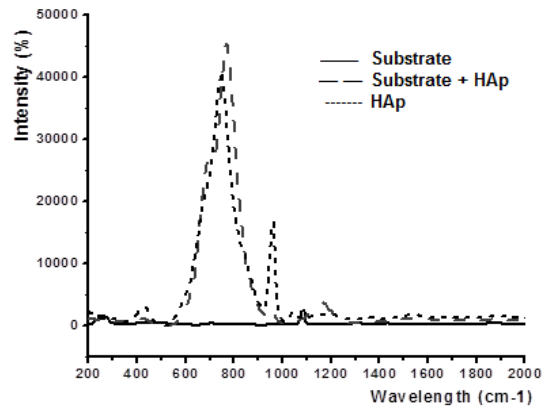


Figure 2. Raman spectra of limestone alone and covered with HAp

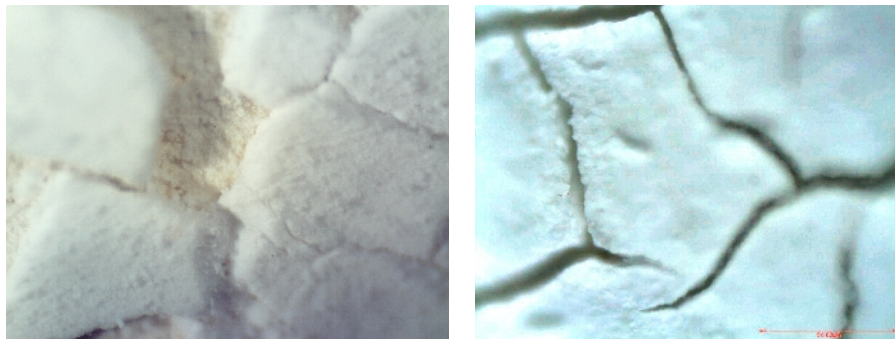


Figure 3. Optical microscopy of limestone surface after a long time after treatment

After treatment with HAp no significant coloristic changes will be observed, this being a proof of beneficial use of HAp (  $E=0.91$  for limestone, 1.65 for travertine and 2.2 for marble).



Figure 4. Travertine treated with HAp

However, as a weathering sign, the chromatic alteration is visible from the chromatic parameters:  $E=3.91$  for limestone, 4.65 for travertine and 3.2 for marble). These indicated that during the degradation, many islands are formed, containing white efflorescence, fragments loss, all together contributing to the coloring of the surface examined sample (Figure 5).

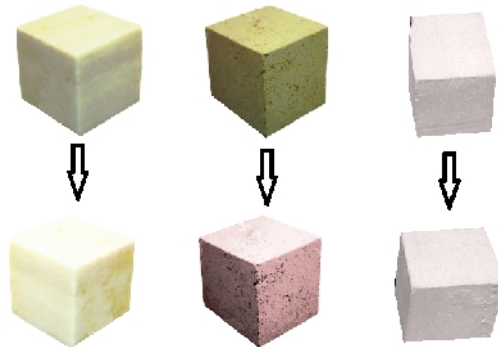


Figure 5. The chromatic aspects of marble (left), travertine (middle) and chalk (right).  
Above are the non-treated samples, and down the treated ones

The samples treated with HAp present a more uniform distribution of the consolidation product and homogeneous infilling of the matrix voids, and induced a slow white colour of the treated surface. Undoubtedly, this is caused by the network of hydroxyapatite, which can bind weathered stone blocks together providing a substantial reinforcement.

## CONCLUSIONS

In this paper the structural, morphological and compositional aspects of some stone samples treated with HAp nanoparticles have been tested. A complex collection of analytical techniques has been used in order to identify the major aspects of restoration with HAp. Some weak bonds are forming between stones and HAp, and a strong

homogeneous consolidation effect was visible, more pronounced for chalk limestone where local white area could be observed, assigned to a stronger interaction, followed by travertine and marble.

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