CHALK STONE RESTORATION WITH HYDROXYAPATITE–BASED NANOPARTICLES

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Abstract
The purpose of this paper is to show the results obtained during chemical investigations of chalk stone materials and their consolidation attempts by using hydroxyapatite (HAp) and strontium hydroxyapatite (SrHAp) nanomaterials.

1. INTRODUCTION
Throughout the history of mankind, the natural stones have been widely used as a material for buildings and monuments. But, in time these natural stones have been affected by several weathering factors [1]. In general, weathering induces different alteration processes for all the building materials, as chemical weathering, which contain the stone solubility or its reactivity with other deterioration factors (air pollutants), and physical weathering, which involves the salt crystallization within the pore structure [2]. Both kinds of weathering lead to many deterioration processes affecting the stone monuments.

Particularly, the stonework with a lime basis is very sensitive to many of deterioration and weathering factors such as soling, pollution, oxidation, air temperature and relative humidity especially in industrial environment [3]. Limestone, mainly composed of calcium carbonate, contains small proportions of other ingredients: silica, clay, iron oxide and magnesium carbonate.

For conservation/restoration of such monuments is necessary to develop materials (micro- and nano) compatible with natural and artificial stone. A novel material that could be effective in consolidating marble is hydroxyapatite (HAp), which has recently been proposed for stone conservation, although for different purposes. HAp was originally conceived as a protective treatment for marble and chalk stone against acid rain [4-7]. The protection offered by HAp is due to HAp lower solubility than calcite.

HAP has also been tested as a consolidating material for porous limestones and sandstones, where it proved to be effective in binding grain boundaries and improving stone mechanical properties [8-10]. In this paper, a preliminary evaluation of HAp efficacy as a consolidating material for chalk stone is presented. Because we observed that Sr is a good element for chalk stone conservation [11], we are testing now SrHAp for stone conservation. The presence of Sr is favouring the calcite stability, is able to interact primarily with the sterically open sites on the surface of calcite during dissolution and that, competition between the precipitation/adsorption of SrCO3 and the dissolution of CaCO3 is occurring at these sites. On the other hand, Sr2+ causes a significant reduction in the growth and dissolution rates of aragonite. This was attributed to reversible adsorption of Sr2+ ions at growth sites (kinks). Cu2+ and Zn2+ could form soluble oxides and carbonated over the calcite surface, while Sc3+ could inhibit the calcite solubilization [12].

Causes of stone deterioration and characterization of building materials, in terms of chemical and physical properties, have been studied in this paper, too. The samples were analyzed by: UV-Vis, FTIR spectroscopy, Dynamic Light Scattering (DLS), XRD, EDXRF, thermal analysis, Scanning electron microscopy (SEM).

Experimental part
Materials
Hydroxyapatite was obtained from Ca(NO3)2×4H2O and (NH4)2HPO4 as Merck commercial reagents [13]. Strontium hydroxyapatite has been synthesized from Sr(NO3)2 and (NH4)2HPO4 [14]. After precipitation, the suspension was kept in digestion for 3 h. The precipitate was then separated by filtration and repeatedly washed with boiling deionized water and dried at 100 °C. The dried powder was manually ground and particles of size <210 nm were separated by sieving.

Equipments
The synthesized materials were characterized through energy dispersive X-ray fluorescence (EDXRF, using a PW4025 MiniPal 2 spectrometer – PAnalytical), X-ray diffraction (XRD, using a DRON UM1 diffractometer, operating at 32 kV and 25 mA, Co Kα radiation - 1.79021 Å), thermal analysis (performed on a TGA/SDTA 851 Mettler Toledo) and Dynamic Light Scattering (DLS - Nano ZS –Red badge).

The samples were analyzed by X-ray diffraction, carried out with a DRON UM1 diffractometer using an iron filter for the CoKα radiation (1.79021Å) and
also, with a XRD, Philips Diffractometer PW 1840, 40kV/20mA, Cu Kα radiation, X-ray fluorescence analysis, performed with an energy dispersive instrument, EDXRF PW4025, type Minipal-Panalytical, with a Si(Li)-detector of 150 eV resolution at 5.89 keV (Mn-Kα-line). The particles size and theirs size distribution have been measured by Dynamic Light Scattering (DLS) technique. For microscopic analysis, scanning electron microscopy (SEM) with Quanta 200 Scanning Electron Microscope (SEM) with magnifications of over 100000x, and atomic force microscopy (AFM), carried out with an Agilent 5500 SPM system, for morphology and 3D topographical images and section analysis. The conservation efficiency of the consolidant was estimated by compressive strength, with Silver Schmidt Hammer L, with a compressive range 5-30 N/mm² and 0.735 Nmm impact energy (EN 12 504-2) and by capillary water uptake tests, determined according to the method according to EN ISO 15148.

Results and discussion
EDXRF results show the lack of impurities in the synthesized materials. The FTIR spectrum presents strong bands, as follows: bands around 600 cm⁻¹, 955 cm⁻¹ and 1020 cm⁻¹ are characteristics for PO₄³⁻. The observation of the asymmetric P-O stretching vibration at 955 cm⁻¹ is a distinguishable peak, together with the peaks around 600 cm⁻¹, correspond to the triply degenerate bending vibrations of PO₄³⁻ in hydroxyapatite, similar to other data presented by the literature [15]. The fact that all FTIR spectra are identical suggests that all the compounds present the same basic structure, respectively the isomorphic substitution on the hydroxyapatite structure. The XRD results, similar to the literature [16] prove the successful isomorphic substitution, a fact not yet mentioned in the literature data, as well as the small dimensions of the synthesized materials (in the nanometric range). Thermogravimetric analysis performed in air shows the endothermic effects accompanying the loss of water through evaporation and dehydration. The absence of other peaks indicates that the synthesized compounds are homogeneous and pure in composition. The analytical results presented above prove the successful synthesis of the hydroxyapatite derivatives.
The conservation efficiency of the consolidant was estimated by compressive strength, with Silver Schmidt Hammer L, with a compressive range 5-30 N/mm² and 0.735 Nmm impact energy (EN 12 504-2) and by capillary water uptake tests, determined according to the method according to EN ISO 15148. The samples treated with HAp present a more uniform distribution of the consolidation product and homogeneous infilling of the matrix voids. Despite of its relatively low stability, HAp is uniform layered, and induced a slow white colour of the treated surface.

For the analyzed samples, the compressive strength determined with Silver-Schmidt Hammer, indicated a compressive strength of 25.33 MPa for the treated sample with HAp, 34.4 MPa for SrHAp, increased values by comparison with the non-treated one (20 MPa). Undoubtedly, this is caused by the network of hydroxyapatite, which can bind weathered stone blocks together providing a substantial reinforcement. SrHAp yielded to increased mechanical properties than HAp (compressive strength), the network between the stone and the nanoparticles suspension being more strong.

The water absorption, measured by capillary water uptake test are also listed in Table 1. The capillary water uptake of the test blocks is decreased after the treatment with consolidants, concluding that the treatment makes the stone samples more compact and less permeable to water. Low capillary action can protect the stone against erosion by water and soluble salts or bases [17,18].

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water absorbed (cc/cm²s)</th>
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<tbody>
<tr>
<td>Not treated</td>
<td>2.22±0.10</td>
</tr>
<tr>
<td>HAp</td>
<td>2.05±0.084</td>
</tr>
<tr>
<td>SrHAp</td>
<td>2.01±0.065</td>
</tr>
</tbody>
</table>

The area treated with HAp have a the low water absorption capacity of these areas with respect to the area treated with SrHAp.

**Conclusions**

In this paper has been treated the structural, morphological and compositional aspects of chalk stone sample prelevated from Basarabi Chalk Church (Romania), for which a new method based on nanoparticles HAp and SrHAp has been tested. A complex collection of analytical techniques XRD, EDXRF, FTIR, thermal analysis, Scanning electron microscopy (SEM), have been used in order to identify the major constituents of chalk stone on this monuments, all these being useful for subsequently method of restoration. Studies have shown to have a higher restoration activity for the compound SrHAp than HAp.
Acknowledgements
This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 222/2012.

4. REFERENCES