

Nanomaterials for Restoration and Conservation of Historical Monuments

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Abstract. The nanomaterials are known as consolidating compatible materials that obey the principle of authenticity historical monuments where they are used. In this paper, hydroxyapatite nanoparticles (HAp) as consolidating nanomaterial, is applied to the chalk samples (without historical value) prelevated from Basarabi historical monument. Some physico-chemical (*Infrared spectroscopy Fourier-Transformed* (FTIR), *Dynamic Light Scattering* (DLS), differential thermal analysis (DSC), *X-Ray Diffraction* (XRD), *Scanning Electron Microscopy* (SEM), *Microscopy Atomic Force* (AFM), relative kinetic stability parameter for the chalk samples treated with HAp, and mechanical properties (compressive strength and capillary water uptake test), have been evaluated and discussed, too, for chalk stone and HAp.

1. Introduction

The materials from the architectural monuments are prone to degradation phenomena, aesthetic, and functional. Historical monuments suffer various forms of degradation, the most common being capillary moisture infiltration combined with migration and crystallization of salts, improper works on architecture structure, vibrations caused by blasting, traffic, cracks in the substrate, corresponding dislocations facing and contraction cracks as a fine network of cracks, due to the contraction of unsuitable materials introduced into the original substrate, technical flaws, the inadequate restoration (refurbishment), the phenomenon of freeze-thaw, air pollution in the presence of humidity and temperature variations, technical defects may result to a friable mortar, resulting in a powdery surface of the plaster, not resistant to mechanical action, deposits adhering impurities (dust, smoke, soot, cobwebs - and adhesion (smoke, tar, bird droppings), due to air pollution, improper maintenance of the monument, soluble efflorescence, poorly soluble or insoluble - are due salts (nitrate, sulfate, chloride,

carbonate) which crystallizes in certain conditions of temperature and humidity on architectural surfaces, and not in the last time, degradations due to the action of microorganisms that thrive in conditions of microclimate: humidity, temperature, light, air pollution [1].

Through their superior properties, the nanomaterials, which became most popular and used materials in architecture conservation, show improved mechanical properties due to the small physical size and a large surface area, known for their compatibility as consolidating materials that obey the principle of authenticity historical monuments that were used [2, 3]. Some nanomaterials as Ca and Mg hydroxides or carbonates, have been applied in the conservation of paper, wood and stone [4, 5].

In this paper, it is studied hydroxyapatite nanoparticles powder (HAp) as an alternative to the above-mentioned hydroxides. HAp is applied to the samples (without historical value) taken from Basarabi historical monument - the first medieval religious monument in Dobrogea. Discovered in 1957, the ensemble Basarabi - Murfatlar is one of the most impressive archaeological sites in Europe. Will be analyzed the size and density of the HAp particles by means of Dynamic Light Scattering (DLS), differential thermal analysis in order to determine the glass transition temperature and the crystallization temperature, *X-Ray Diffraction* (XRD) and *Scanning Electron Microscopy* (SEM) and *Microscopy Atomic Force* (AFM) to identify the phases and microstructures present. Also, the petrographic and physico-chemical (X-ray fluorescence energy dispersive (EDXRF), relative kinetic stability parameter for chalk samples treated with hydroxyapatite compared to those treated $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, are discussed in this paper. Mechanical properties as compressive strength and capillary water uptake test, have been evaluated and discussed, treated as shown above.

2. Experimental Part

Specimens Samples Preparation

The samples prelevated from Basarabi Church (samples collected from the exterior of the monument, without any value for this church. Samples were obtained by taking a minimum part of the archaeological object, with the aid of a scalpel with diamond tip, to minimize any damage and contamination. Being detached from the Church's wall, all the samples, have the same constitution as the wall and the same composition.

Consolidants

Hydroxyapatite was obtained 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 [6]. The powder was dry mortar in a mortar and pestle and then calcined in alumina crucible at 1200°C for 1h.

Application of Consolidants

The application of all types of consolidant was carried out by spraying, 5 times. After the each treatment the samples were covered for one day by a slightly opened cover to avoid quick evaporation of solvent. Next day the cover was removed and the specimens were exposed to laboratory conditions to get dry. The following application cycle was done when the specimens became completely dry. After drying the specimens were obviously covered by white layer of nanomaterial suspension.

Characterization Techniques

The samples were analyzed by using the following techniques:

Ion Chromatography, performed on a DIONEX DX-500 Chromatograph, was used to identify the soluble salts as cations and anions present in the samples. The eluent was sodium carbonate and sodium bicarbonate with a flow rate of 2 ml/min, and a 4 mm column for the separation of anions.

The diffraction analysis has been carried out in a DRON UM1 diffractometer using an iron filter for the CoK_α radiation (1.79021 Å) and also, with a XRD, Philips Diffractometer PW 1840, 40 kV/20 mA, Cu K_α radiation).

DSC was performed on a Mettler-Toledo Instrument DSC 823°. Samples (1-2 mg) were loaded into sealed aluminum pans with lids and heated to 600°C at a heating rate of 10°C min⁻¹ in oxygen flux (100 ml min⁻¹).

The phases were also characterized by **Fourier transformed infrared spectroscopy** (FT-IR, Perkin-Elmer Spectrum One FT-IR Spectrometer), using the KBr pellets method.

For evaluating the effectiveness of the consolidating treatments, the **relative kinetic stability** of the dispersion of nanomaterials, was defined as ξ , which is calculated after [7].

The particles size and theirs size distribution have been measured by **Dynamic Light Scattering** (DLS) technique.

Scanning electron microscopy (SEM) produces high resolution images of a sample surface. The Quanta 200 Scanning Electron Microscope (SEM) was used to produce enlarged images of a variety of specimens, achieving magnifications of over 100000x providing high resolution imaging in a digital format.

Atomic force microscopy (AFM) investigations were carried out with an Agilent 5500 SPM system, described by PicoSPM controlled by a MAC Mode module and interfaced with a PicoScan controller from Agilent Technologies, Tempe, AZ, USA (formally Molecular Imaging). The original images for the samples, the 3D topographical images and section analysis over the articles were

performed using the PicoView SPM Software, version 1.6.2, Molecular Imaging. Height image data obtained by the AFM is three-dimensional.

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).
- by capillary water uptake tests, determined according to the method according to EN ISO 15148 .

3. Results and Discussion

Stone Characterization

Stone materials are characterized by a mineral-inorganic nature, and by hydrophilic properties, both these aspects being very important when choosing the treatments for their conservation. Two main causes for stone deterioration have to be mentioned: acid attack (caused by rains and humidity condense in polluted urban atmospheres) and soluble salts cyclic crystallization [8]. The first mechanism (acids) induces corrosion to carbonatic materials such as calcium and/or magnesium carbonates based stones while silicatic stones are only poorly affected. The second mechanism (salts) is mainly active towards porous stones, independently of their nature. Also, important is the effect on low porosity stones. This is important for the consolidation of natural stone such as limestone, marble or sandstone as well as for mortar and plaster [9].

It should take into account that decay agents can reach the surface both from outside (acid attack and salts deposits) and inside (soluble salts), in case of porous materials [10]. Some studies on environmental influences on degradation stone monuments, considering the factors such as temperature (average, minimum, maximum), number of days of frost and sunny days, humidity annual average rainfall amount and chemical composition, currents air, will be evaluated, too, knowing that carbonates have been detected as the predominant in the body of the church with sulphates impurities [11].

Usually, calcium carbonate is occurring as limestone, chalk and biomaterials. It is known that some nonaqueous dispersions of calcium, barium or magnesium hydroxide nanoparticles started to be tested and used as new possible consolidants for calcareous material [12]. Gypsum is, as lime, one of the important component used as binder alone or together with lime for the production of plaster and mortars [13, 14]. In order to evaluate the efficiency of the new treatment method, based on nanomaterials, first of all the characteristics of the substrates and chalk wall, have been evaluated.

Many literature sources rank magnesium sulfate among the most damaging salts [15] The alteration of stone is a natural and irreversible process. Crystallization of soluble salts in the construction materials, is considered today one of the most important decay process. These soluble salts induce the rock fabric, when

efflorescence appear, especially, and induce crystallization within the pores causing the stone damage. All the damage processes from the stone surface is due to high level of sulphates, chlorides, nitrates, detected by ion chromatography and Ca, Na, K and Mg. Deterioration of mortar can be rarely attributed to the presence of only one salt. The most abundant salts are chlorides, sulphates or nitrates, of calcium, sodium, potassium, magnesium and sometimes also ammonium kations. Source of chlorides are usually deicing agents, nitrates are of organic origin. Sulphates are usually rising from groundwater but may be also a product of calcium carbonate corrosion reaction with sulphur oxides. By ICP-MS all the metals constituents of the chalk sample, have been identified, Table 1.

Table 1. The metal composition of the chalk stone sample [20]

Metal	Concentration (ppm)	Metal	Concentration (ppm)
Ti	75.19	Cu	42.69
Sr	857.69	K	2600
Ba	136.92	Al	8100
Mn	272.115	Fe	4800
Bi	191.69	Mg	2300
Sn	152.115	Na	8600
Si	14400	Li	34.61
Ca	241200	Zr	10.77

Divalent metal ions of similar ionic radius as Ca^{2+} may be incorporated as impurities into calcite during mineral precipitation. In agreement with the literature data, these results indicate the presence of Sr, which is favouring the calcite stability by precipitation/adsorption of SrCO_3 and the dissolution of CaCO_3 is occurring at these sites [16]. On the other hand, Gutjahr and co-workers have shown that Sr^{2+} causes a significant reduction in the growth and dissolution rates of aragonite. This was attributed to reversible adsorption of Sr^{2+} ions at growth sites (kinks) [17]. Cu^{2+} and Zn^{2+} could form soluble oxides and carbonated over the calcite surface [18].

Magnesium sulfate tends to precipitate within a wider crystallization front and in pores of different size, while sodium sulfate is mainly concentrated close to the surface and in large pores. The goal of the DSC experiments was to determine the composition of the salt mixture that forms by drying a magnesium sulfate solution [19–21]. By DSC techniques is important to detect the soluble salts arising from the degradation, because the soluble salts are usually hydrated, so they

undergo changes at low temperatures, less than 100°C, Fig. 1. Hydrus or anhydrous Mg and Na sulphates are visible in all chalk samples.

Table 2. Decomposition temperature of the salts which appear as products of the monument chalk stone

Soluble salts/ T(°C)	Phase transition
Na ₂ SO ₄	275
Na ₂ SO ₄ • 10H ₂ O	90; 271
K ₂ SO ₄	583
MgSO ₄	352
MgSO ₄ • 7H ₂ O	135; 200; 360
MgSO ₄ • 6H ₂ O	110; 156; 200; 275; 360
MgSO ₄ • H ₂ O	345
(NH ₄) ₂ SO ₄	355
KNO ₃	133

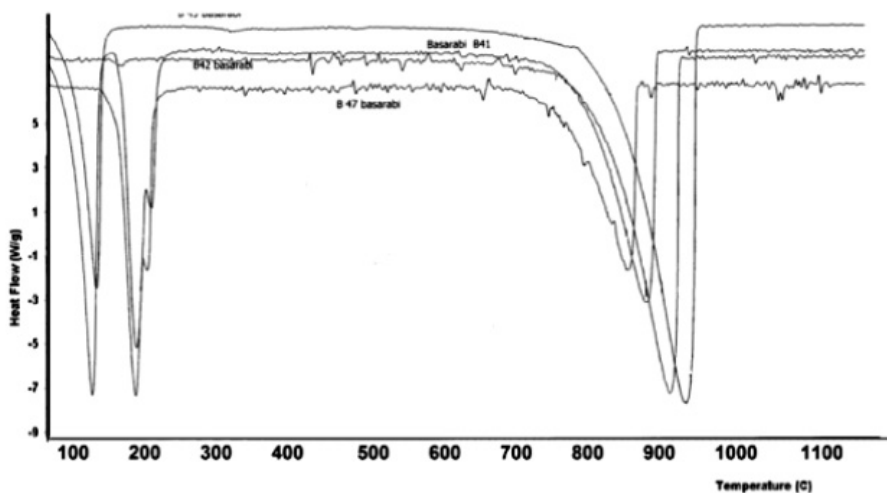


Fig. 1. The DSC diagrammes for different church walls (left ordonate, mg; right ordonate, mg/Celsius degree). [B41 = stone dislocated from inside West wall; B42 = wall efflorescence dislocated from the inside wall surface; B45 = wall sample from inside East wall; B47 = dust from the dome surface].

The FTIR spectra of HAp put into evidence the specific absorption bands:
 - two bands at 3432 cm⁻¹ and 622 cm⁻¹ due to the stretching mode of hydrogen-bonded OH⁻ ions and hydrogen-bonded OH⁻ ions, respectively,

- the bands from $600\text{--}601\text{ cm}^{-1}$ and 571 cm^{-1} , 1090 cm^{-1} , $1050\text{--}1044\text{ cm}^{-1}$ arises from -PO_4^{3-} ,
- the bands at 632 cm^{-1} attributed to OH- group.

The SEM images put into evidence the crustalites and only few spherical agglomerations of $0.1\text{ }\mu\text{m}$, Fig. 3.

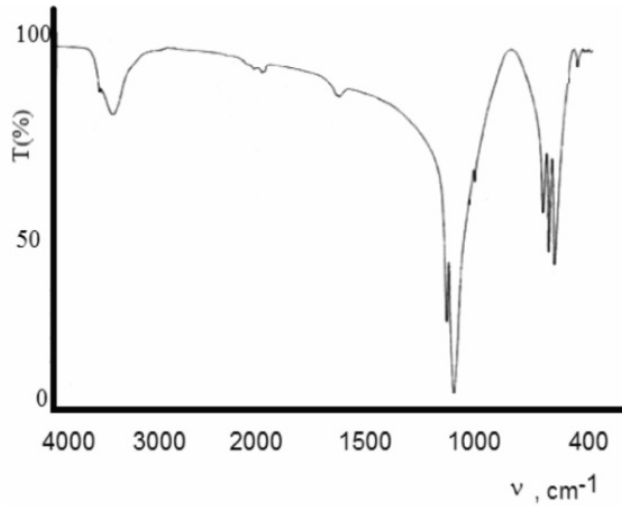


Fig. 2. FTIR spectrum of Hap.

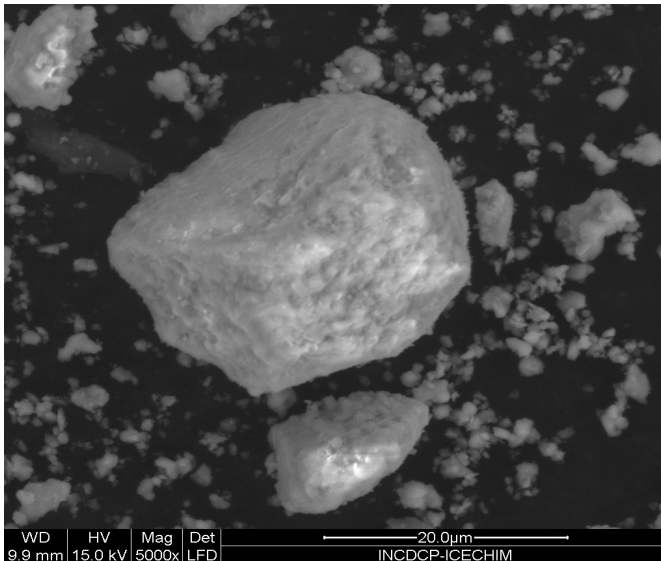


Fig. 3. SEM of Hap.

From AFM topography is easy to observe a good distribution around 100 nm, Fig. 4.

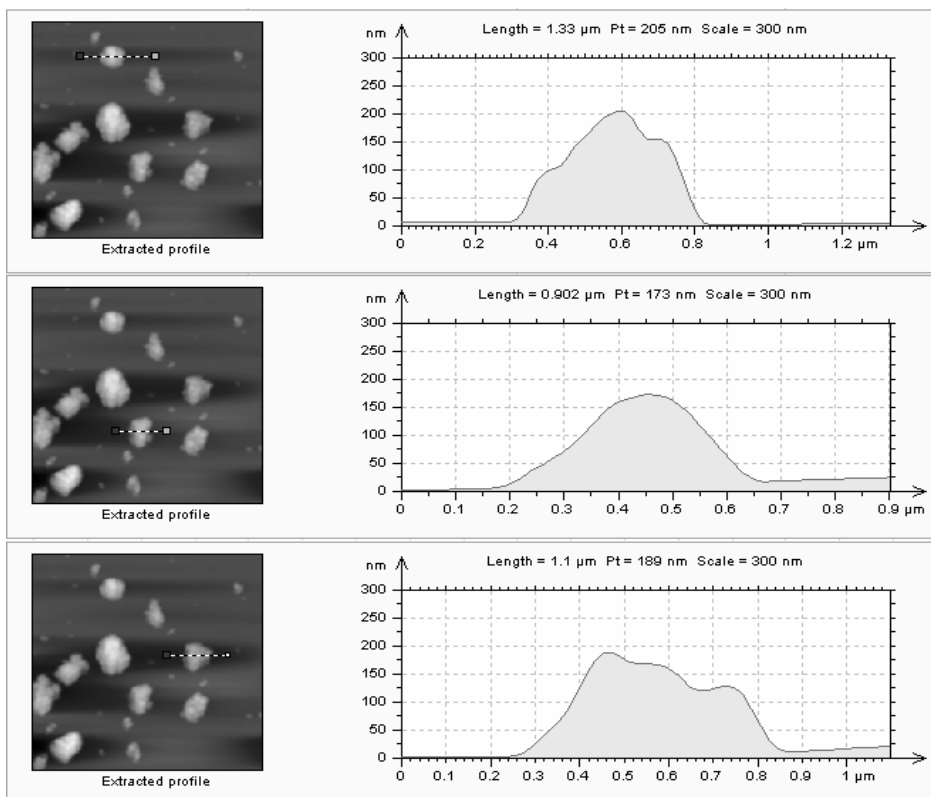


Fig. 4. AFM for Hap.

Consolidation Options

Nanotechnology applied to building materials represents an example of nanotechnologies application based on the design of material properties in order to obtain the increased performances, developing new products for specific architectural applications. Historically, limestone objects, lime-based renders and wall paintings have been treated with solutions that resulted ultimately in the deposition of calcium carbonate [22]. A saturated solution of calcium hydroxide in water was one of the earliest treatments for building materials and was well documented in the classical literature by authors such as Vitruvius (c. 70–25 BC) [23, 24]. For chalk consolidation, HAp has been used, due to the similarities with calcite of the lattice parameters, Table 3.

Table 3. Lattice parameters of calcite and calcium hydroxide [14]

Mineral	a (Å)	b (Å)	c (Å)
Calcite	9.98	9.98	33.82
Hydroxyapatite	9.45	9.44	6.90

In order to avoid the long time of consolidation, a new nanomaterial has been used, selected from its similarity of lattice parameters with those of calcite and proper to consolidate carbonate stones [25].The relative kinetic stability of HAp has a low value (30 nm, Fig. 5), by comparison with calcium hydroxide which has a bigger size (408.9 nm), Figs. 6.

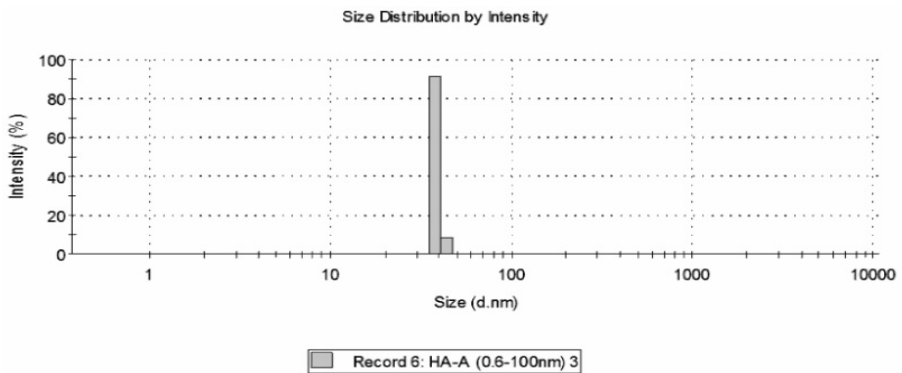


Fig. 5. Size distribution for HAp nanoparticles dispersed in 2-propanol.

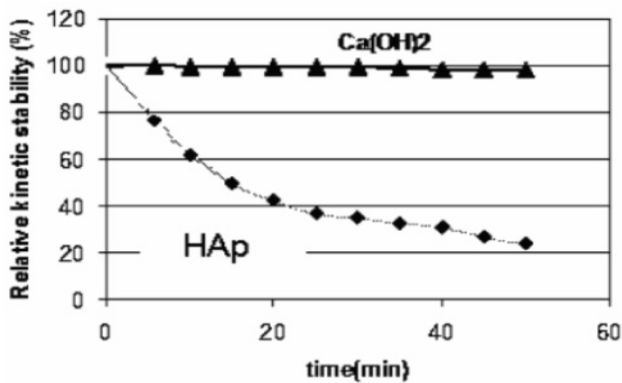


Fig. 6. The relative kinetic stability of nanomaterials.

Scanning electron microscopy research was performed to investigate microstructure characteristic of the samples, Fig. 7. An encapsulation and covering

of acicular chalk crystals with size around 8 microns could be observed, and also, is visible a good consolidation capacity.

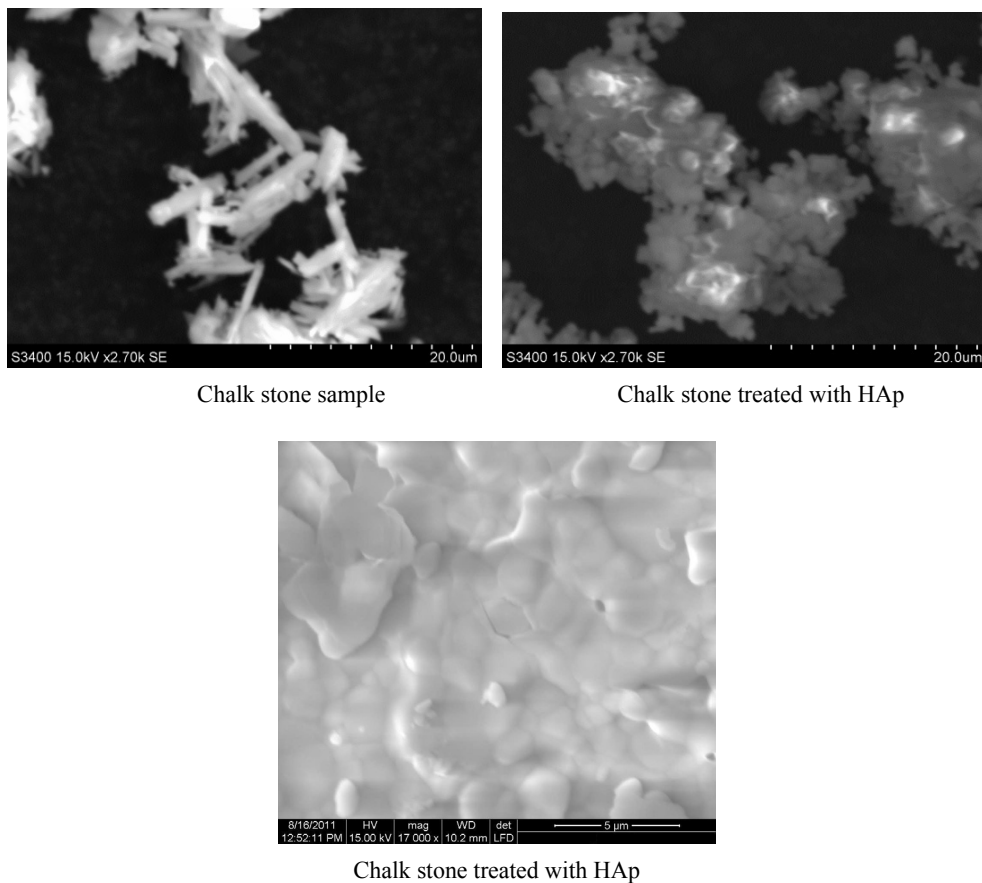


Fig. 7. SEM of chalk stone, HAP and chalk treated with Hap.

Similar results have been obtained by AFM, Fig. 8. AFM revealed a rough surface architecture for HAp, the predominant size of grains being in the range of 90–100 nm. The light part of the image can be the consequence of the presence of a thick part of sizing material, possibly to an aggregate form [27]. By spraying on a cubic piece, whiter colour is evident, Fig. 9.

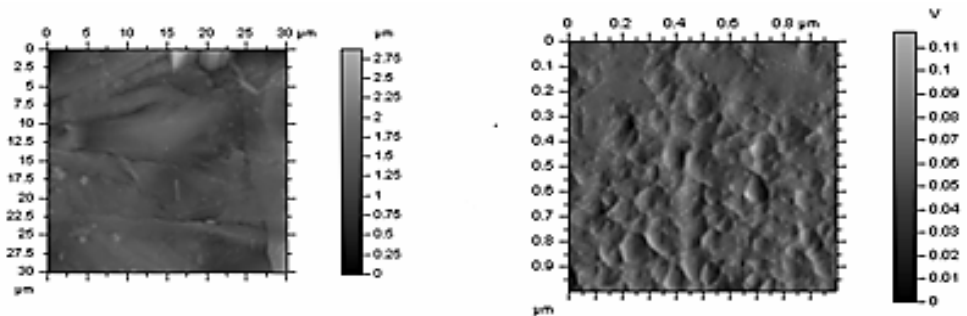


Fig. 8. AFM image of $\text{Ca}(\text{OH})_2$ on chalk surface (left), and HAp on chalk surface (right).

Three specimens of cube shape ($4 \times 4 \times 4 \text{ cm}^3$) of chalk samples were used for measurement. Before testing, all samples were dried up to constant weight at 80°C in a drying chamber for 24 hours. After the drying process the substrates were left to get cold for two hours in a dessicator and their aspect was measured, Fig. 9. Despite of its relatively low stability, HAp is uniform layer, and induce a high white colour of the treated surface.

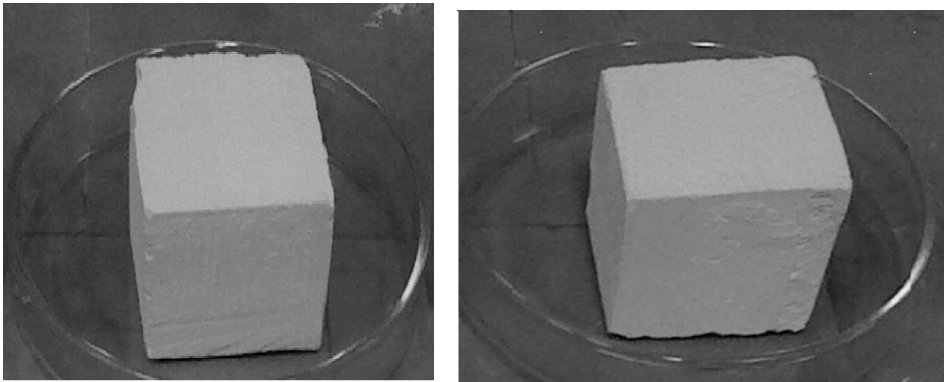


Fig. 9. The aspect of chalk sample before (left) and after treatment (right) with nanomaterial HAp.

For the chalk samples, the compressive strength determined with Silver-Schmidt Hammer, indicated that the most effective treated sample has a compressive strength of 40 MPa and is that treated with $\text{Ca}(\text{OH})_2$. In the case of $\text{Ca}(\text{OH})_2$, we have to take into account the non-uniform thickness of the consolidant, due to the aggregation tendency of $\text{Ca}(\text{OH})_2$. The results are shown in Table 4. For the chalk samples, the treatment with $\text{Ca}(\text{OH})_2$ do not cause any increase in cohesion, rather a decrease. Also, to explain the low values obtained with HAp, we should take into account the considerable moisture from this area, which lowered the average value of compressive strength of this area.

Table 4. Mechanical tests for the studied samples

Sample	Treatment	Compressive strength (Silver Schmidt) (MPa)(5 mm)	Water absorbed (cc/cm ² s)
Chalk sample	Not treated	20±3.2	2.22±0.10
	Ca(OH) ₂	40±2.3	2.25±0.22
	HAp	25±2.5	2.05±0.084

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, Table 4. Low capillary action can protect the stone against erosion by water and soluble salts or bases [28]. The area treated with Ca(OH)₂ shows an absorption capacity bigger to the untreated zone. A possible explanation of this behaviour is the inhomogeneity of the chalk and the high capacity of Ca(OH)₂ to aggregate.

4. 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 restoration method based on nanoparticles HAp has been tested. A complex collection of analytical techniques DLS, SEM, AFM, DSC, XRD, ξ , have been used in order to identify the major constituents of chalk stone, useful for subsequently method of restoration. The mechanical parameter compressive strength and capillary water uptake, concluded the efficiency of HAp by comparison with Ca(OH)₂.

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