

NANOMATERIALS FOR THE CONSERVATION AND PRESERVATION OF HISTORICAL MONUMENTS

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ABSTRACT

For conservation/restoration of historical buildings and monuments it is necessary to develop new materials (micro- and nano) compatible with natural and artificial stone. Due to their improved optical and mechanical properties (due to quantum effects and small physical size coupled with a large surface area, respectively), the nanomaterials are recognized as consolidating compatible materials that obey the principle of authenticity for historical monuments. The new recently developed consolidants based on calcium hydroxide (Ca(OH)₂), magnesium hydroxide (Mg(OH)₂) and hydroxyapatite (HAp) nanoparticles, dispersed in alcohols, are treated in this paper as an alternative for conservation of a historical/religious monument (Ensemble Basarabi – Murfatlar). Discovered in 1957, this monument is one of the most impressive and unique archaeological sites in Europe. Situated on a chalk cliff, it is very sensitive to moisture, frost, salts, all these being recognized as the most important and common causes of monument degradation. Calcite (the variety of calcium carbonate detected) dissolution is affected by the presence of foreign compounds, Mg²⁺ (from MgSO₄ • 7H₂O and MgSO₄ • 6H₂O) and Na⁺ (from Na₂SO₄ • 10H₂O and Na₂SO₄), being the major cations in seawater and groundwater. Also, vaterite, an unstable rock, contributes to chalk degradation, absorbing negatively charged species (the anion SO₄²⁻ from atmospheric pollution, and transforming calcite into gypsum); the non-charged species are absorbed by calcite. Some detailed petrographic and physico-chemical (X-ray fluorescence energy dispersive (EDXRF), thermal analysis, X-ray diffraction (XRD), Dynamic Light Scattering (DLS), Atomic force microscopy (AFM), relative kinetic stability parameter) of some real and model samples treated with HAp compared with those treated with Ca (OH)₂ and Mg (OH)₂ are also presented. We applied all these nanomaterials on real samples, cut into cubes (4x4x4 cm³) from boulders detached from the Church's wall and of no particular value. Up to now, we have not applied the new solutions directly onto the monument, because we have to evaluate exactly the long term effect of the nanomaterials on this monument.

Keywords

Nanomaterials, calcite, hydroxyapatite, conservation

1. Introduction

For conservation/ restoration of historical buildings and monuments it is necessary to develop materials (micro- and nano) compatible with natural and artificial stone [1, 2]. Inorganic consolidants (calcium hydroxide, magnesium hydroxide, barium hydroxide) are commonly used in restoration and conservation treatment. However, the low solubility of calcium hydroxide in water (1.7 g • l⁻¹) and the low stability of lime dispersions in water make these consolidants of little effect. The new recently developed consolidants based on hydroxyapatite, calcium hydroxide and magnesium hydroxide nanoparticles dispersed in alcohols, are discussed in this paper. The consolidation effect was checked by measuring several physical, chemical and microstructure characteristics. All the experiments from this paper have been carried out for the first time in the literature, in Basarabi Church, Ensemble of Churches located in the south-east part of Romania [3]. For this reason the paper is original and novel. From a historical point of view, this monument occupies a very special place in Romanian old art, however, in terms of time, it is one of the first medieval religious monuments from Dobrogea, Romania. The discovery, made by chance in 1957, revealed an Ensemble being formed by a church, chapels and other relatively numerous rooms and galleries, revealing the life style at the end of the tenth century and the beginning of the eleventh century. These rudimentary attempts at cave art and architecture, of constructive and aesthetic experiences, are like similar constructions in other parts of the Empire Byzantine, as well as, in part, the Steppe regions and Northern Europe. The main monument, the church, like the chapels, galleries and funeral spaces, has a design and decoration that is an obvious attempt to be artistic, though extremely awkward in terms of technique. It was probably the work of some local craftsmen, working for a monastic group where they had had found temporary shelter near Dobrogea around or after the time of the Byzantine conquest. The religious monument consists of the usual Orthodox worship spaces - narthex, nave and altar - the latter complete with a semicircular apse, the first two chapels being covered by a barrel vault dome carved in the chalk like the altar and chapels. The decoration of these monuments is chalk scratching on the walls - at least two stages, the first of which is represented by the superficial incisions, the second through some deep incisions - of Christian symbols, some Cyrillic, Glagolitic and runic inscriptions, some attempts

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at anthropomorphic representations, and other religious, symbolic or profane images, all characterized by a certain aesthetic criteria.

Nowadays, this historical building is highly degraded, requiring fast and efficient solutions for restoration. Situated on the cliff of a chalk hill, this ensemble is built from calcium carbonate (chalk) and is very sensitive to humidity, frost, salts etc. Atmospheric pollution and acid deposition materials are recognized as the most important and common causes of decay in heritage monuments [4]. Usually, calcium carbonate occurs as limestone, chalk and biomaterials. It can adopt three polymorphs forms: calcite, aragonite and vaterite [5]. It is known that calcite (the variety of calcium carbonate detected by XRD) dissolution is affected by the presence of foreign substances Mg^{2+} (from $MgSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 6H_2O$) and Na^+ (from $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4), being the major cations in seawater and groundwater [6]. Also, the anion SO_4^{2-} (from pollution-related atmospheric SO_2) favours calcite conversion to gypsum and is responsible for stone wall solubilization. Causes of stone deterioration, the mechanisms, type of building materials, in terms of chemical and mineralogical composition, the physical, chemical and mechanical properties, are all studied in this paper. The samples were analyzed using X-ray diffraction (XRD), energy-dispersive X-ray fluorescence (EDXRF), thermal analysis (TG), Dynamic light scattering (DLS) and microscopy (Scanning electron microscopy (SEM), Atomic force microscopy (AFM)). The materials' compatibility with restoration - conservation of the monument will be carried out by techniques such as zoom microscopy, SEM and relative kinetic stability.

2 Materials

2.1 Specimens samples preparation

For our experiments, **real samples** have been used, cut into cubes ($4 \times 4 \times 4 \text{ cm}^3$) from boulders detached from the Church's wall and of no particular value. h. Up to now, we have not applied the new solutions directly on the monument, because we have to evaluate exactly the long term effect of the nanomaterials on this chalk stone monument.

2.2 Consolidants

Nanosuspensions of $Ca(OH)_2$ and $Mg(OH)_2$, respectively, dispersed in ethanol (25g particles per litre of ethanol), have been synthesized in the lab [7]. Hydroxyapatite was obtained by chemical precipitation method from calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$ and dibasic ammonium phosphate $(NH_4)_2HPO_4$, 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 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. After drying, the specimens were obviously covered by white layer of nanomaterial suspension.

2.3 Characterization techniques

The real samples have been analysed by the following

analytical techniques:

Petrographical analysis was carried out with a Leica DM750 P polarizing microscope, and Olympus BX-40 microscope with infinity optics system. All these microscopes have various attachments for fluorescent-light microscopy, digital photo-micrography, 35-mm color film photo-micrography, Polaroid photo-micrography, and examinations in both transmitted and reflected-light modes.

The diffraction analysis was carried out in a DRON UM1 diffractometer using an iron filter for the CoK_α radiation (1.79021\AA). Also, the mineralogical composition of the stone was determined by powder X-ray diffraction (XRD, Philips Diffractometer PW 1840, 40kV/20mA, $Cu K_\alpha$ radiation) which was employed to identify the crystalline phases present in the films.

Thermal analysis was performed on a Mettler Toledo Thermo-gravimetric Analyzer TGA/SDTA 823^o, in the range of temperature 25°C to 1000°C , in dynamic air, with 60 ml/min, at a heating rate of $10^\circ\text{C}/\text{min}$, in alumina crucible, for all the paper samples, of 3mg to 5mg. DSC was performed on a Mettler-Toledo Instrument DSC 823^o. Samples (1-2 mg) were loaded into sealed aluminum pans with lids and heated to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ in oxygen flux ($100 \text{ ml} \cdot \text{min}^{-1}$).

ICP-OES have been recorded with a specialized Spectrometer Optima 2100 DV ICP-OES System (Perkin Elmer).

X-ray fluorescence analysis was 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-K α -line). A Rh-tube with an acceleration voltage of 50 kV and a primary filter of Pd with 0.05mm thickness were used for excitation.

For evaluating the effectiveness of the consolidating treatments, the relative kinetic stability of the dispersion of nanomaterials, was defined as ξ , which is calculated using eq.1 [8].

The particles size and theirs size distribution were measured by Dynamic Light Scattering (DLS) technique with Zetasizer instrument and a computer with the Zetasizer software. The software is used to control the measurement of the sample.

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 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).

ICP-MS elements analysis was recorded with a spectrometru Optima 2100 DV ICP-OES System (Perkin Elmer, with the

following characteristics: fully computerized dual-view, can use any wavelength in the radial, axial or mixed viewing modes in a single method, automatic dual-view system which ensures added lowest detection limits and the larger working areas application, multi-element analysis, detect and quantify more than 70 elements.

3 Results

In order to know exactly the effect of the nanomaterials on the monument, we applied different analytical techniques to investigate the real chalk samples, taken from the surrounding of the monument.

3.1 Analysis of real chalk samples

3.1.1 Petrographical analysis

From a petrographic point of view, the chalk sample is a clay bioclastic limestone (chalk), mainly composed of calcium carbonate ($\text{CaCO}_3 = 91.4\%$) and small amounts of quartz. It has a highly porous microstructure, with quite coarse pores. The chalk sample has both an organogenic chemical structure, with calcite (and/or vaterite) and minerals clay as constituents, and an autigens chemical structure with iron oxides and hydroxides, and a bioclastic foraminiphra, diagenesis local recrystallization of calcite (Figure 1).

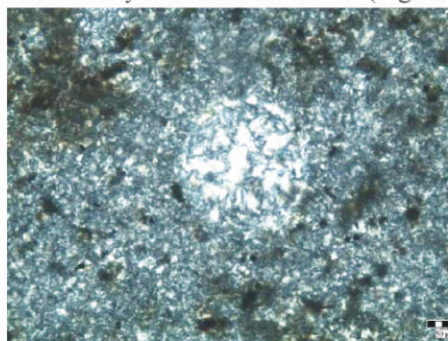


Figure 1 Petrographic image of real chalk sample.

The petrographic microscopy investigations of the samples confirm the same conclusion from the literature: vaterite, which is very unstable (stable only under 10°C) has the tendency to form framboidal structures, in the presence of CO_2 . These framboidal structures are aggregations of smaller, mostly spherical, particles, with an average size of these elementary spheres comprised between 36 and 150 nm (Figure 2).

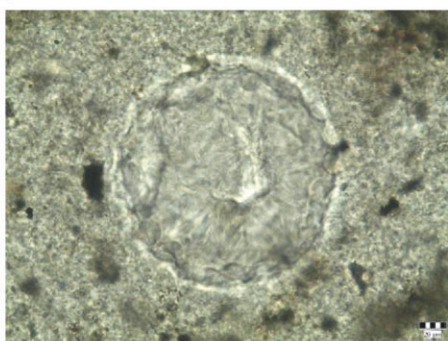


Figure 2 Image of a framboidal aggregates of vaterite from real chalk sample.

3.1.2. Metal composition (ICP-OES and EDXRF)

The chalk sample contain a lot of metals (Ti, Sr, Ba, Mn, Bi, Sn, Cu, K, Al, Fe, Mg, Na, Si, Ca, Li, Zr), the presence of Sr, favouring the calcite stability, being able to interact primarily with the sterically open sites on the surface of calcite during dissolution [11,12]. Sr^{2+} causes a significant reduction in the growth and dissolution rates of aragonite [13].

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

Table 1 The metal composition of the real chalk sample.

Similar results with those of ICP-MS, has been obtained by EDXRF, but only for the metals in concentration greater than 10 ppm, Figure 3.

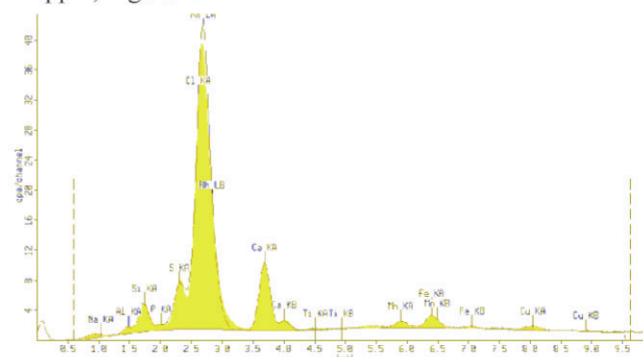


Figure 3 EDXRF spectrum of the chalk sample.

3.1.3. XRD results

XRD investigations revealed the same calcite and vaterite species present in the sample. Vaterite is highly unstable when exposed to water. This could be the cause for higher vaterite/calcite ratio at the inside sample, and a lower vaterite/calcite ratio for the outside sample. XRD calibration graphs were constructed using the 104 reflection of calcite, and the 110 reflection of vaterite (Figure 4).

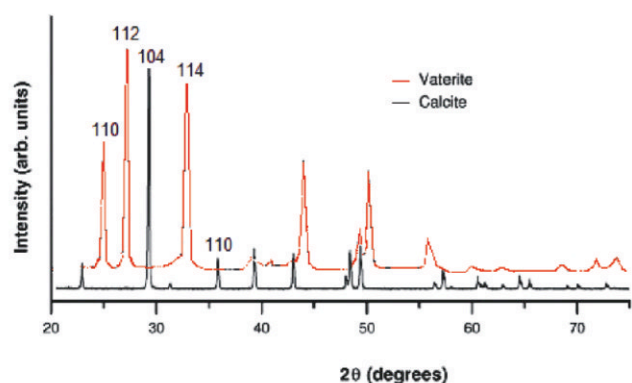


Figure 4 The XRD graphics for vaterite and calcite from real chalk sample

3.1.4 Thermal analysis

From our experimental thermal analysis, it has been concluded that the soluble salts arising from the degradation undergo changes at low temperatures, less than 100 °C. Sulphates, nitrates and phosphates undergo phase transition under 600 °C, identified by DSC techniques, hydrous or anhydrous Mg and Na sulphates being the most frequent. Two phases are stable at room temperature: an anhydrous phase: thenardite (Na_2SO_4), and a decahydrate phase: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Mirabilite only exists under $\sim 32^\circ\text{C}$. In our samples, mirabilite appears visible, but it is possible that it is thenardite which transformed into mirabilite through a large number of freeze-thaw cycles.

3.1.4 Relative kinetic stability

For the nanoparticles suspension, the relative kinetic stability for every type of nanomaterial was determined, Figure 5. Kinetic stability and particle size distribution analysis of nanoparticles is a measure of settling speed and particle (cluster) size of the tested nanomaterials. For a good nanomaterial, a kinetic stability should be long enough to maintain all the particles well dispersed. These dispersions can be easily used for application by brushing or complete immersion of the samples in the calcium hydroxide nanoparticles dispersion. Decreasing the particle size is accompanied by the increase of the surface area.

Calcium hydroxide has the best kinetic stability, in comparison with magnesium hydroxide and hydroxyapatite. This finding could be correlated with the nanoparticles size. Despite the fact that calcium hydroxide has a bigger size (408.9 nm, determined by DLS) (Figure 6a), it has a good kinetic stability, most probably due to its aggregation capacity, followed by $\text{Mg}(\text{OH})_2$ (Figures 6b), and hydroxyapatite, with a very small size (30 nm) (Figure 6c). Dimensional analysis of hydroxyapatite particles was made in isopropyl alcohol, by using an agate grinding in the presence of alcohol, after the samples were ultrasonicated for 5 min in an ultrasonic bath (35kHz). Dispersions acquired a white opalescent appearance. Hydroxyapatite does not aggregate.

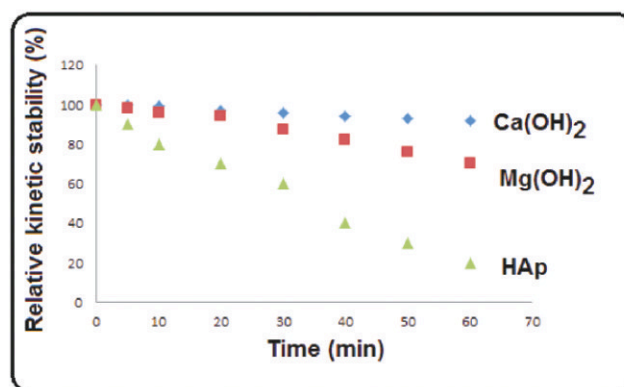


Figure 5 The relative kinetic stability of nanomaterials used for real chalk samples treatment.

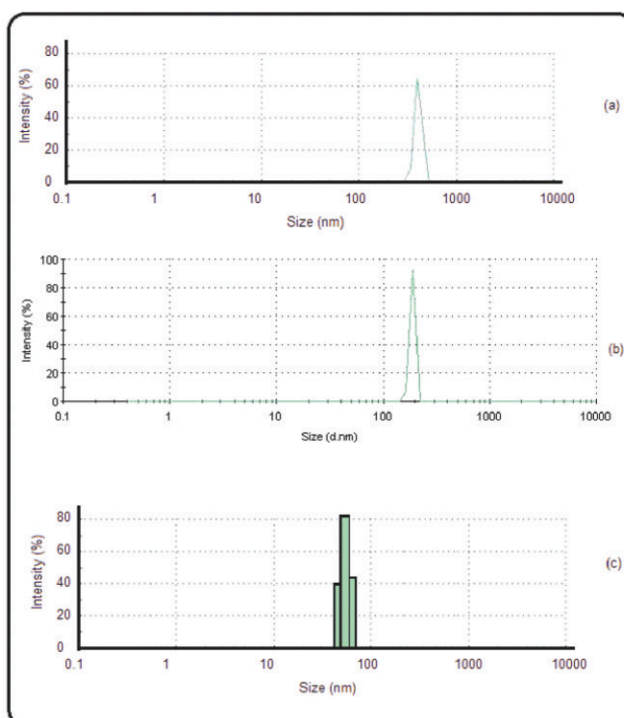


Figure 6. Size distribution for $\text{Ca}(\text{OH})_2$ (a), $\text{Mg}(\text{OH})_2$ (b) and hydroxyapatite (c) nanoparticles dispersed in 2-propanol.

But, instead of its low relative kinetic stability, HAp has a good covering capacity, as it is shown by SEM, in Figure 7.

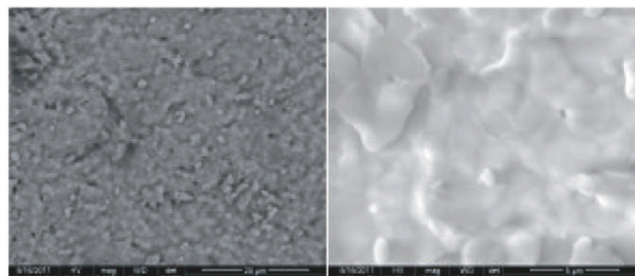


Figure 7 SEM of HAp 5000x (left) and 17000x (right).

Meanwhile, AFM revealed a rough surface architecture for HAp, the predominant size of grains being in the range of 90-100 nm and more than 100 nm for $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. In order to study the effect of the nanoparticles on chalk real samples, we applied these nanomaterials suspensions on model

samples and studied with AFM microscopy. For $\text{Ca}(\text{OH})_2$ and HAp, a higher magnification of 5000x was used to provide a greater depth to the field and to aid to morphological and topographical analysis of the sample, as in Figures 8-10.

The samples treated with HAp present a more uniform distribution of the consolidation product and homogeneous infilling of the matrix voids. Three samples of cube shape ($4 \times 4 \times 4 \text{ cm}^3$) were used for measuring. After the drying process the substrates were left to get cold for two hours in a dessicator and their aspect was measured, Figure 11.

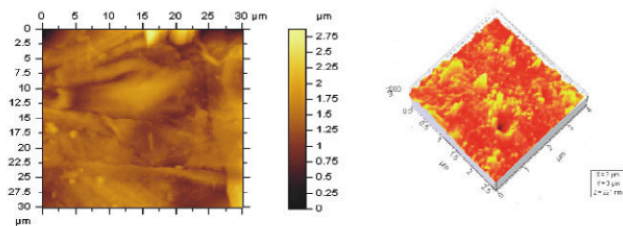


Figure 8 AFM image of $\text{Ca}(\text{OH})_2$ on surface obtained in contact mode (a), 3D AFM image of $\text{Ca}(\text{OH})_2$ on surface (b).

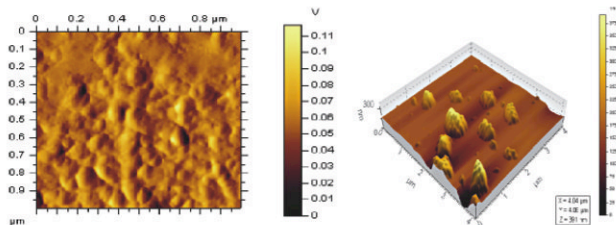


Figure 9 HAp sprayed on the surface (tapping mode) (a), 3D AFM morphology for HAp nanocrystals on surface (b).

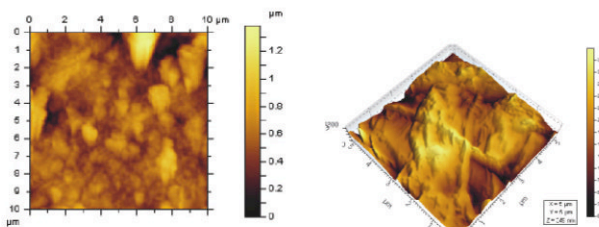


Figure 10 AFM image of $\text{Mg}(\text{OH})_2$ on surface obtained in contact mode (a), 3D AFM image of $\text{Mg}(\text{OH})_2$ on surface (b).

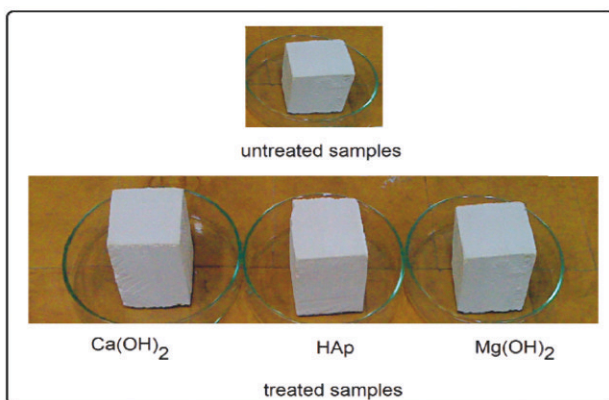


Figure 11 The aspect of the real chalk sample not treated (up) and treated with nanomaterials (down).

3.1.5 Compressive strength

The compressive strength of the real chalk samples treated with nanomaterial suspension, were determined with Silver-Schmidt Hammer, as the best method for consolidation, and indicated that the most effective treated sample has a compressive strength of 25 MPa and the one treated with HAp. The results are shown in Table 2.

Table 2 Drilling resistance tests for the studied samples

Sample	Treatment	Compressive strength (MPa)
Chalk sample	Not treated	20 ± 3.2
	$\text{Ca}(\text{OH})_2$	18 ± 1.3
	HAp	25 ± 2.5
	$\text{Mg}(\text{OH})_2$	17 ± 2.2

4. Discussion

The conservation of building materials in historic monuments are among the subjects of importance at international level. Usually the stone conservation processes involve operations such as diagnosis, cleaning, consolidation and protection. For protection, some nonaqueous dispersions of calcium, barium or magnesium hydroxide nanoparticles have started to be tested and used as new possible consolidants for calcareous material [9]. In order to improve the efficiency of this consolidation method, new nanomaterials have to be used and evaluated.

From a petrographical point of view, the real sample resembles vaterite. Its mineralogy on the surface of the chalk samples identified vaterite 70-75%, calcite 8-15%, and accessory inclusions of portlandite, quartz, dolomite and pyrite. At the deeper 1467-1470 m interval vaterite is less common (25%) and calcite (63%) probably replaced vaterite; quartz, portlandite, and dolomite are present in minor amounts. Petrographic examination reveals a light-brown core of high relief surrounded by a colourless rim of low relief. Samples from the 1467-1470 m intervals have a thick core and thin rim, whereas in those from the 1263-1270 m interval the core is thin, even lacking, and the rim is thick. The petrographic microscopy investigations of the samples confirm the presence of vaterite, which is very unstable (is stable only under 10 °C) and has the tendency to form framboidal structures, in the presence of CO_2 . These framboidal structures are aggregations of smaller, mostly spherical, particles, with an average size of these elementary spheres comprised between 36 and 150 nm [10]. These framboidal aggregates have been identified in the real chalk samples, taken from Basarabi Curches.

For evaluating correctly the composition of the real chalk samples, ICP-OES analysis were carried out, concluding that the chalk sample contains a lot of metals (Ti, Sr, Ba, Mn, Bi, Sn, Cu, K, Al, Fe, Mg, Na, Si, Ca, Li, Zr), the presence of Sr, favouring the calcite stability, able to interact primarily with the sterically open sites on the surface of calcite during dissolution [11,12]. Sr^{2+} causes a significant reduction in the growth and dissolution rates of aragonite [13]. Divalent metal ions of similar ionic radius as Ca^{2+} may be incorporated as impurities into calcite during mineral precipitation. The concentrations of trace metals, e.g., Mg,

Sr or Ba, in biogenic calcite are used as palaeo-proxies for the reconstruction of past environmental conditions ([14]), while sorption to calcite could be an alternative pathway for the immobilization of hazardous metals, e.g., Cd and other radionuclides [15]. In agreement with the literature data, these results indicate the presence of Sr, which favours the calcite stability, being able to interact primarily with the sterically open sites on the surface of calcite during dissolution and that, like the situation for Mn, competition between the precipitation/adsorption of SrCO_3 and the dissolution of CaCO_3 occurs 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, while Sc^{3+} could inhibit the calcite solubilization [18]. In fact, Sc^{3+} wasn't identified in our stone.

The chemical species adsorbed are entirely different between vaterite and calcite, that is, negatively charged species on vaterite, and non-charged species on calcite. The surface of calcite is negatively charged (proper for metallic cations adsorption), and the vaterite surface is positive and thus the adsorption of negatively charged species (anions, for example SO_4^{2-}) is reasonably explained [19]. Vaterite can recrystallize to calcite within 20 to 25 h at room temperature [21, 22]. The presence of vaterite and calcite and their ratio inside and outside of the monument have been identified by XRD.

A higher vaterite/calcite ratio for the inside sample, and a lower vaterite/calcite ratio for the outside sample, could be identified due to the instability of vaterite in aqueous solution, and its capacity to be transformed within a short period of time into calcite or aragonite (depending on temperature) [20].

The deterioration process of limestone involves the dissolution and recrystallization of calcium carbonate [23]. Crystallization damage caused by highly soluble salts, such as sodium chloride and sodium sulfate, is usually manifested by powdering and crumbling of the stone's surface. Less soluble salts such as calcium sulfate form glassy, adherent films which cause spalling of a stone's surface. There most damaging salts are sodium sulfate (as the anhydrous salt thenardite (Na_2SO_4) or the decahydrate mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) [24]. Thenardite increases in volume by more than three times upon conversion to mirabilite, and it has been argued that this growth in volume was the cause of so-called —hydration damage [25]. Salts in the stone may be of different chemical composition and origin.

Another parameter for evaluating the danger of salts is their hydration properties. As already mentioned, $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite) is an extremely soluble salt and according to a previous explanation is a dangerous salt. It derives from the hydration of NaSO_4 (thenardite), and increases in volume by about 400%. The slightly soluble salts do the most damage as they expand below the surface and can push the surface off. Very soluble salts usually crystallize at the surface and can be brushed off. The insoluble salts stay either on or below the surface [26].

The most important aspect of the consolidation of real chalk

samples, are the inorganic consolidants, because they are more durable, even though they are not able to improve the mechanical properties of the stone. When inorganic consolidants are used, any improvement of weathering behaviour should be entrusted to the protective system, otherwise deterioration will start again.

Some properties of conservation materials can be improved with the presence of nanomaterials [27]. In this paper, we discuss the application of some nanomaterials on real chalk samples, taken from Basarabi Church, samples collected from the exterior of the monument, detached from the Church's wall. We evaluated the nanomaterials as a surface-protective layer for chalk in order to obtain a noticeable retardation of the weathering.

The humid environment and the high and large porosity of this stone favour the consolidation over time, and these conditions must be taken into account when nanoparticles are used to consolidate carbonate stones [18]. The performance of HAp has already been proven in restoring the strength of weathered limestone [10]. Other researchers have also investigated the use of HAp as a consolidant [28–31]. Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, has a much lower solubility and dissolution rate with the ability to confer protection in acidic environments, with a dense coating of only about 10 μm .

Due to the large surface area the reactivity increases and this leads to better physico-chemical properties (comparing to the bulk materials) such as strength, stability of dispersions and higher active material content (more concentrated) [32].

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. A considerable increase of white degree can be observed after treatment with nanomaterials, and with HAp, especially. Despite its relatively low stability, HAp is uniform layered, and induced a high white colour of the treated surface.

Undoubtedly, the consolidation with inorganic consolidants are the most adequate, that with HAp being the most efficient, with the highest value for compressive strength. This is caused by the network of hydroxyapatite, which can bind weathered stone blocks together providing a substantial reinforcement. In the case of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, we have to take into account the non-uniform thickness of the consolidant, due to the aggregation tendency which is more pronounced for $\text{Ca}(\text{OH})_2$. In the case of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$, smaller values were obtained, due to their aggregation tendency and the inhomogeneity of the chalk stone.

5. Conclusions

This paper has discussed the structural, morphological and compositional aspects of chalk stone samples taken from Basarabi Chalk Church (Romania), for which a new method based on nanoparticles HAp was tested.

A complex collection of petrographic and analytical techniques ((Dynamic Light Scattering (DLS), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), Energy-dispersed X-ray fluorescence (EDXRF), X-ray diffraction (XRD), relative kinetic stability parameter

(ξ), were used in order to identify the major constituents of chalk stone (metals, anions, type of calcium carbonate), the influence of environmental salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4) on this monuments, all useful information for the subsequent method of restoration.

The petrographic microscopy investigations of the samples coupled with XRD concluded the presence of vaterite outside of the church (stable only under 10°C and with a tendency to form framboidal structures, in the presence of CO_2), possibly responsible for further damage to the stone (open framboidal structure).

The AFM observations of the samples treated with the HAp show micro-sized clusters of calcitic formations; the distribution and morphology of these nanostructured particles show a homogeneous consolidation film. The consolidation film is characterized by the presence of plate-like nanoparticles that aggregate into micro-sized clusters, which are compact and polydispersed. On the other hand, specimens treated with HAp present a more uniform distribution of the consolidation product and homogeneous infilling of the matrix voids.

The mechanical parameter compressive strength, determined by Silver Schmidt hammer, indicated the highest value for HAp. This is caused by the network of hydroxyapatite, which can bind weathered stone blocks together providing a substantial reinforcement. In the case of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$, smaller values were obtained, due to the aggregation tendency of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$, the inhomogeneity of the chalk stone, and the humidity, determined here by capillarity water uptake.

HAp seems to be the best consolidant for chalk samples, it is not toxic, and is recognized as a biocompatible biomaterial.

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