



MORTAR PE BAZĂ DE NANOMATERIALE PENTRU CONSERVAREA FAȚADELOR CONSTRUCȚIILOR NANOMATERIALS-BASED MORTARS FOR BUILDING FAÇADES PRESERVATION

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In the field of architectural restoration, ancient materials and their decay in aggressive environments are studied, through case-histories. Some properties (capillarity, porosity) are tested on different façade surfaces, in order to identify the existing materials and to select the proper materials useful for restoration. The achieved microscopy (MO, AFM) studies allow observing the presence of the main weathering signs and the previous consolidation results. The EDXRF and ICP-AES techniques offer informations about the elemental composition of sample, while GC-MS allow the identification of the previous coniferous resins from the glue used for restoration. The identification of mainly of terpenes and derivative patterns highlighted the presence of plant oils and pine resins. Also, the CIELAB color parameters are a proof of the efficacy of the conservation process. Moreover a comparison between traditional mortars (based on cement) and those based on nanomaterials (calcium hydroxide, hydroxyapatite and their controlled mixture) used in restoration are investigated in this paper.

În domeniul restaurării arhitecturale, prin intermediul unor studii de caz sunt analizate materialele vechi, precum și dezintegrarea lor în medii agresive. Unele proprietăți (capilaritate, porozitate) sunt testate pe diferite suprafețe de fațadă, în scopul identificării materialelor constituente și selecției materialelor utile în restaurare. Studiile de microscopie (MO, AFM) realizate permit observarea principalelor semne de alterare și a rezultatelor consolidării cu diverse materiale. Tehnici precum EDXRF și ICP-AES oferă informații asupra compoziției elementale a probei, în timp ce GC-MS permite identificarea rășinilor de conifere din adezivii utilizați anterior pentru restaurare. Identificarea terpenelor și a derivaților acestora evidențiază prezența uleiurilor vegetale și a rășinilor de conifere. De asemenea, parametrii de culoare CIELAB reprezintă o dovadă a eficacității procesului de conservare. În plus, în această lucrare este investigată comparația dintre mortarele tradiționale (pe bază de ciment) cu cele bazate pe nanomateriale (hidroxid de calciu, hidroxiapatită și amestecul lor controlat) utilizate în restaurare.

Keywords: nanomaterials, façade presertvation, analytic characterization

1. Introduction

For conservation/restoration of different buildings from national/international patrimony, different materials have been used, many of them being from regional raw materials [1]. In this way, there is a polemic discussion about the type of the materials used for restoration materials, either traditional materials (stone, brick, wood, mortar and plaster) and new innovative materials (polymers, resins, concrete), taking into account their huge applicability and aesthetic value, and their short lifetime [2]. Among the historical mortars, gypsum, lime and lime pozzolana have been used as binding materials. As aggregate material, river sand, pebbles, brick pieces and powder have been used together with hay, horse hair, goat hair which have served as fibers [3].

Depending on the building substrates, the restoration mortars were different, and in this paper we will discuss a study case - the Ensemble Basarabi, dated IX-XI centuries. The Basarabi Chalk Churches Assembly is part of the Roman career, part of the hill Tibișir on the outskirts of Murfatlar (Basarabi), 20 km before Constanța. This rupester monument includes churches, galleries branched vaults, housing the tombs [4]. The stone is chalk, amorphous calcium carbonate, almost pure, soft, with high porosity and very hygroscopic. After discovery in 1957 and 1958, the monument supported different conservation/restoration operations, some of them being completely negative:

1. A protective concrete construction was partially completed and the rest of the monument remains in front of advanced degradation induced by weather variations in temperature and humidity,

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and other factors responsible for compromising the monument [5].

2. A temporary protective building, wooden, covered with roofing felt complemented its repaired later in 2006, roofing felt is replaced with polycarbonate enclosures, to remove excessive moisture protection [6].

3. In addition, the lake formed during construction of the Danube-Black Sea Channel, rich in salts and a slightly alkaline pH accelerates the degradation of the monument [7].

4. The restorations performed over time were not based on scientific studies of compatibility and polymeric resin added to restorative solutions has done worse accelerating the degradation process [8].

In this paper, some properties of limestone (chalk facade surfaces), have been measured in order to identify the existing materials and to select the proper materials useful for restoration. Different techniques have been used in order to evaluate the existing damages and the solutions for future restoration procedures: microscopy studies, EDXRF and ICP-AES for elemental composition, while GC-MS, FTIR and Raman spectroscopy for identification of the coniferous resin from the glue used to restoration and CIELAB color parameters. Moreover, a comparison between traditional mortars (based on cement) and new materials (based on nanomaterials – calcium hydroxide, hydroxyapatite and their controlled mixture) used in restoration are investigated.

2. Materials and characterization techniques

The chalk samples taken from the monument (detachable sample without the architectural value) were analyzed by the following analytical techniques:

X-ray diffraction analyses were performed using a Rigaku SmartLab equipment, operating at 45 kV and 200 mA, using Cu K α radiation (1.54059 Å).

Fluorescent X-ray energy dispersive (EDXRF) was performed with a PW4025 EDXRF instrument type MinIP - PANalytical, detector resolution Si (Li) - 150 eV at 5.89 keV (Mn - K α - line).

Light Optical Microscopy (LOM) has been recorded by using NOVEX microscope with a Leica EC3 camera under a magnification of 40x to 600x.

Scanning electron microscopy (SEM) has been recorded with the Quanta 200, 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, with a PicoScan controller from Agilent Technologies, Tempe, AZ, USA (formally Molecular Imaging). Trace elements were quantified using **ICP-AES** (inductively coupled plasma-atomic emission) spectrometer Varian Liberty 110 Series,

with multielement, matrix matched standards for the quantitative determinations. The **porosity** measurements have been achieved with an instrument from Quantachrome, NOVA 2200E. Instrument measurement error is $\pm 5\%$. The samples were degassed for 3 hours at 300 °C under a pressure of 0.334 MPa in a nitrogen atmosphere. The surface area was calculated by applying the BET equation and distribution by pore size was determined based on the BJH model.

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 [9].

Color measurements, achieved with a spectrophotometer (Carl Zeiss Jena M40) under a D65 light source and an observer angle of 10°. 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 differences in ΔL^* , Δa^* , and Δb^* and the total color differences ΔE^* between treated and non-treated samples were calculated [10].

Gas-chromatography with mass spectrometry (GC/MS) has been achieved with GC/MS Triple Quad Agilent Technology (for compounds identification we based on NIST Library). *GC method*: Column DB-WAX (L=30m, D=250 μ m, d=0,25 μ m; Oven Program: 50°C for 5min., then 4°C/min to 150°C, then 10°C/min to 320°C; Carrier gas: He, Flow=1ml/min; Injector Temp.: 250°C; Injection Volume: 0,5 μ l. *MS Method*: QQQ Collision Cell: Quench Flow Gas (He) = 2,2 ml/min; Collision Flow Gas (N₂) = 1,5 ml/min; Type of Source : EI; Electron Energy : 70 eV; Source Temperature: 230°C ; Aux Temp2. : 280°C ; Scan Segment : 40-400; Type of Chromatogram : TIC

2.1. Consolidants and application

Nanosuspension of Ca(OH)₂ is supplied as CaLoSiL E25 consisting of 25g particles per litre of ethanol. Hydroxyapatite was obtained by chemical precipitation method from calcium nitrate tetrahydrate Ca(NO₃)₂·4H₂O and dibasic ammonium phosphate (NH₄)₂HPO₄, at room temperature. The powder was dried and then calcined in alumina crucible at 1200 °C for 1h. The mixture Ca(OH)₂ : HAp (30g/l Ca(OH)₂ + 15g/l HAp) has been obtained by suspending the individual powders into isopropanol as solvent.

3. Results and discussion

In 2003-2005, the construction reached a limit stage, rainwater entered the large amounts through damaged roofs and evaporation was "strangled". Were accumulated many proliferated

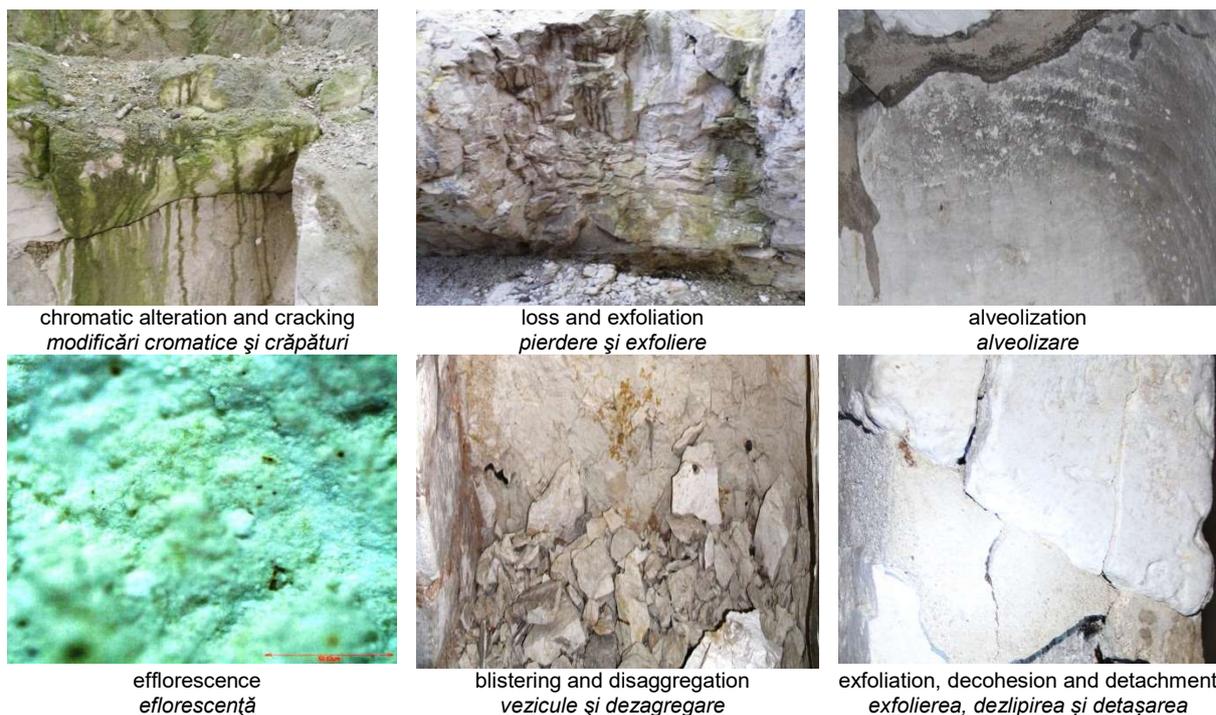


Fig. 1 – Representative images of the deterioration aspects of Basarabi churches
Imagini reprezentative pentru deteriorarea bisericuțelor de la Basarabi.

biological colonies (bacteria, fungi, algae, mosses, lichens, etc.) and salts and the decomposition products of these organisms, have been crystallized and produced significant deterioration by chemical action and mechanical dismantling (granular degradation and incised surfaces are among the most serious) [11]. All these chalk deterioration are visible in Figure 1.

It is known that humidity inside porous materials, can cause structural damage and aesthetic, structural degradation of constituent materials of the monument, in cold conditions, after freeze-thaw phenomenon. The salts of the efflorescence phenomena encountered in the walls are sulfates, carbonates, and nitrates (sodium, magnesium, calcium and potassium). Among the most aggressive salts include: thenardite (Na_2SO_4) or mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Thenardite increase in volume more than three times by converting the mirabilite, or the increase in volume is the main cause of damage by moisture [12]. From compositional point of view, the walls belonging to Basarabi Ensemble contains a number of metals (Ti, Sr, Ba, Mn, Bi, Sn, Cu, K, Al, Fe, Mg, Na, Si, Ca, Li, Zr), the presence of Sr^{2+} (in spite of their radioactive hazard potential) is favoring the stability of calcite, being able to interact primarily with free sterically hindered position from the surface of the calcite. Also, Sr^{2+} causes significant reduction in the formation and dissolution of aragonite. Cu^{2+} and Zn^{2+} may form soluble oxides and carbonates on the surface of calcite, while Sc^{3+} can inhibit calcite solubilization [13]. From mineralogical point of view,

the chalk surface contains vaterite (70-75%), calcite (8-15%) and numerous inclusions (Portland, quartz, dolomite and pyrite) [14]. Vaterite is highly unstable when exposed to water; it can recrystallize to calcite at room temperature (20 - 25 h), and at higher humidity [15]. This is the cause for higher vaterite/calcite ratio inside of the monument, and a lower vaterite/calcite ratio outside [16]. Meanwhile, the native calcite particles have negative zeta potentials in the presence of some organic compounds (pollutants accumulated inside) [17], being responsible for the accumulation of cations (metals) higher outside than inside [18].

3.1. Treatment with traditional mortar (based on concrete)

As a traditional solution, the treatment with mortar is the worst solution for this monument, due to ettringite (E) and thaumasite (T) in the wall filler sample, concomitant with a decrease of calcite [16]. These species could be identified in XRD diagram at the following 2θ (degree): 40; 50, 55, 60, 68, 76, 80.

Thaumasite, $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}](\text{SO}_4)(\text{CO}_3)$ or $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$, or $\text{Ca}_6[\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 (\text{SO}_4)_2 (\text{CO}_3)_2$, is formed from external sulfate attack of cement concrete at low temperatures [16]. Thaumasite tends to form at low temperatures (4 °C - 10 °C), in the presence of water. The presence of sulfate induces the formation of ettringite with aluminium provided by the cement. Sulfate can be supplied from the chalk damaged surfaces (gypsum), and carbonate can be supplied from atmospheric CO_2 or from limestone present in the concrete or mortar.

Table 1

Adsorption/desorption parameters of N_2 / Parametrii pentru adsorbția/desorbția N_2

Sample	Medium diameter of pores (nm)	Specific surface (m ² /g)	Pore volume (cm ³ /g)	Size (nm)
Chalk sample	2.988	8.672	0.017	100
Chalk +HAp	3.125	5.745	0.013	70
Chalk +Ca(OH) ₂	2.969	10.288	0.017	30
Chalk +HAp:Ca(OH) ₂	3.132	19.763	0.031	50



Fig. 4 - Optical microscopy of micro-sized clusters of calcitic formations formed on chalk / *Imagine microscopică a clusterelor de formațiuni calcitice formate la suprafața cretei.*

The FTIR shows overlapped of the chalk groups [CO_3^{2-} (1426, 1085, 876)], with those of HAp [PO_4^{3-} bands (470, 568, 602, 964, 1041 and 1093 cm^{-1}), with those consolidants $Ca(OH)_2$ [1390 cm^{-1} and 866 cm^{-1}]. In addition, we observed some specific changes in the spectrum (wider bands) after the treatment with $Ca(OH)_2$:HAp and new peaks appeared in the region possible assigned to CaHAp [24].

Despite of its relatively low stability, the mixture $Ca(OH)_2$:HAp is uniform layer, with uniform depth of penetration, and don't induce a significant whiter colour of the treated surface (Figure 9).

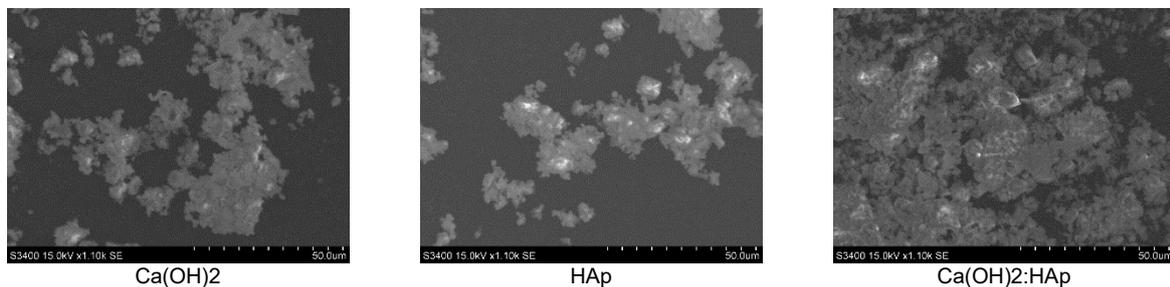
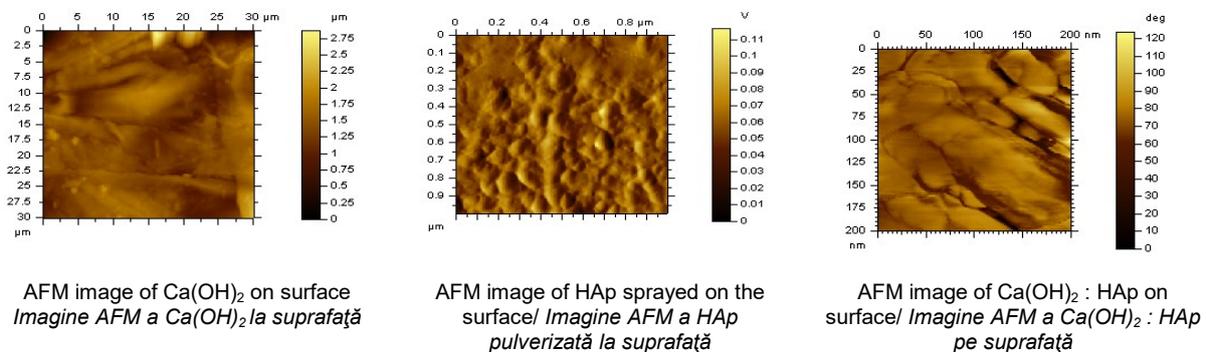


Fig. 5 - SEM images of images of $Ca(OH)_2$: HAp by comparison with the individual components. *Imagine SEM a $Ca(OH)_2$: HAp comparată cu imaginile probelor individuale.*



AFM image of $Ca(OH)_2$ on surface
Imagine AFM a $Ca(OH)_2$ la suprafață

AFM image of HAp sprayed on the surface/
Imagine AFM a HAp pulverizată la suprafață

AFM image of $Ca(OH)_2$: HAp on surface/
Imagine AFM a $Ca(OH)_2$: HAp pe suprafață

Fig. 6 - AFM images of $Ca(OH)_2$: HAp by comparison with the individual components
Imagine AFM a $Ca(OH)_2$: HAp comparată cu imaginile probelor individuale.

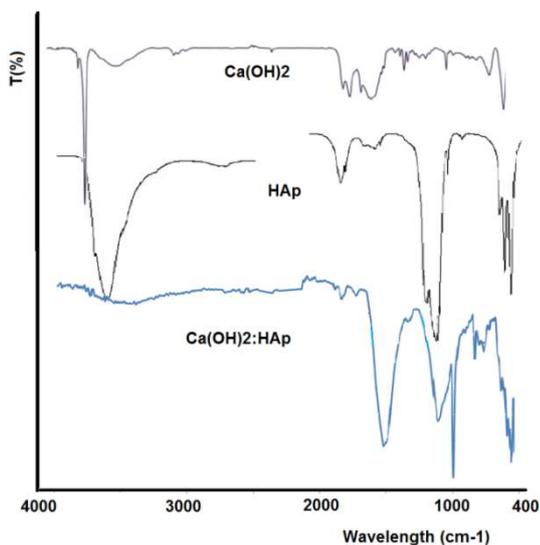


Fig. 7 - FTIR spectra of all used consolidants.
Spectre FTIR ale consolidanților folosiți.

One of them is water absorption, measured by capillary water uptake test. 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 (2.22 (cc/cm²s) at non-treated sample to 2.61 (cc/cm²s) at treated one with Ca(OH)₂:HAp).

4. Conclusions

In this paper has been compared a traditional method of stone restoration (based on cement) with a new one based on nanomaterials (based on nanoparticles Ca(OH)₂:HAp), evaluating the structural, morphological and compositional aspects of chalk stone sample prelevated from Basarabi Chalk Church (Romania). If the treatment with cement led to a continuous degradation due to ettringite and thaumasite formation (induced by gypsum), the product HAp : Ca(OH)₂ shows a homogeneous consolidation film, characterized by the presence of plate-like nanoparticles that aggregate into micro-sized clusters, compact and

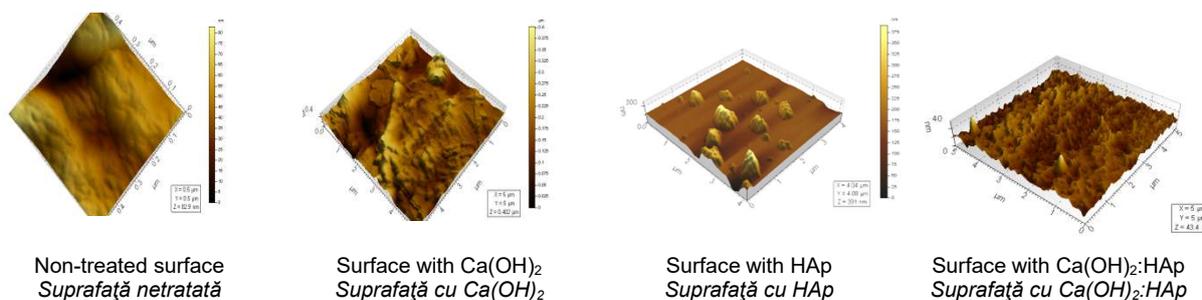


Fig. 8- The AFM images of treated surface for depth penetration / Imagini AFM ale suprafețelor tratate (adâncime de penetrare).

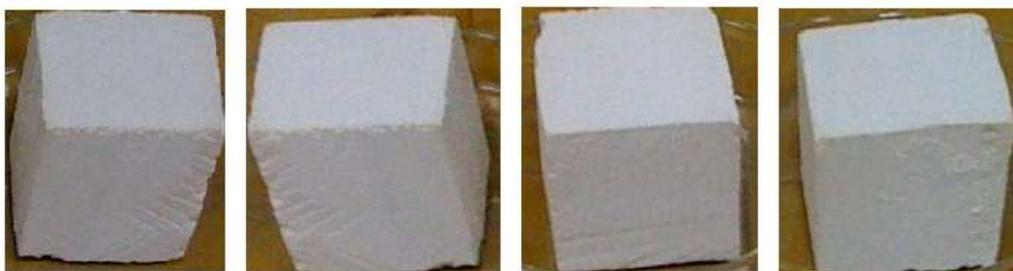


Fig. 9 - The color of the chalk samples (from left to right: chalk untreated, chalk+Ca(OH)₂; chalk+HAp; chalk+Ca(OH)₂:HAp).
Culoarea probelor de cretă (de la stânga la dreapta: cretă netratată, cretă+Ca(OH)₂; cretă+HAp; cretă+Ca(OH)₂:HAp).

Contrary, for hydroxyapatite treated samples the b* values decrease to 1.05 for non-treated sample and to 1.14 for treated sample with HAp and 1.18 for the case Ca(OH)₂:HAp. The compressive strength determined with Silver-Schmidt Hammer, indicated that the most effective treated sample has a compressive strength of 20.33 MPa and is the case of HAp: Ca(OH)₂, due to the network between hydroxyapatite with chalk stone, providing a substantial reinforcement [20-25].

polydispersed, with an homogeneous infilling of the matrix voids. The compressive strength, and the capillarity water uptake indicated us the optimum values for HAp: Ca(OH)₂.

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