

In Vitro Compatibility of Hydroxyapatite Nanoparticles (HAp-NPs) for Restoration Purposes of Archaeological Lime-Based Plasters

Hussein Marey Mahmoud

Department of Conservation, Faculty of Archaeology, Cairo University, 12613 Giza, Egypt

email: marai79@hotmail.com, ORCID: <https://orcid.org/0000-0002-1598-1580>

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Abstract. For a number of years, nanomaterials have been considered as a perfect solution to maintain the stability of different cultural heritage materials. In the present trial, hydroxyapatite nanoparticles (HAp-NPs) have been synthesized via the wet chemical reaction of calcium nitrate and diammonium phosphate. Then, the possible efficiency of HAp-nanoparticles was evaluated to improve restoration formulas for some archaeological lime-based plasters. A broad series of analytical methods, namely OM, FE-SEM, TEM, AFM, XRD and BET surface area-pore size analysis, was selected for characterizing the archaeological samples and to rate the experimental tests. Further, the physical-mechanical behavior of samples was measured. The emulated modifications induced by the HAp-NPs treatment have been evaluated and discussed.

Introduction

Historical literature data claim that lime-based mortars and plasters were first used by the ancient Greeks, while the significant development in lime production was made by the Romans in the 2nd-century BC [1]. In the Pharaonic era, limestone powder (CaCO_3) together with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) have been identified randomly in wall plasters in many tombs and temples. As for Roman mortars, natural or artificial pozzolanic additives were used to create an effective hydraulic nature which explains the superb behavior of these mortars [2-4]. Similarly for the Coptic period, an extensive application of lime-based plasters used to uniform the walls of tomb-chapels and monasteries was also reported.

In general, the stability of ancient plasters is substantially affected by several inducing factors. Effectively, the non-uniform structure of the multi-components plasters plays an influential role in the weathering process. The reaction of each individual crystal with the surrounding atmospheric conditions is partially or completely different compared to other components of the same object. For different types of monuments, the impact of saline solutions, high levels of relative humidity and the variations of air temperature have been recorded. It is well examined that salt weathering gives rise to the deformation of material's microstructure [5]. This effect is a key factor influencing the material's durability as a result of material's loss and the accretion of porosity [6]. As a matter of fact, the long-term conservation plans for carbonate-based materials is one of the most insistent issues for conservators. Offering a sufficient compatibility to the original substrate and forming a durable protective layer are major targets [7].

Taking into account that the traditional acrylic-based polymeric coatings achieve a low durability to the treated materials, while the silicate-based ones induce only a physical bonding [8]. For enough years, a large number of nanomaterials has been applied to build up a desirable durability for carbonate monuments and a self-protection against weathering factors. As a leading material used for conservation, nanolime $\text{Ca}(\text{OH})_2$ has shown significant results in improving the mechanical strength of lime-based structures [9-12]. Following these aims, many advantages of other nanomaterials such as titanium dioxide nanoparticles (TiO_2 -NPs) have been experienced. The research of La Russa et al. [13] showed a quite well effectivity of an aqueous formula of titanium dioxide nanoparticles, dispersed in an acrylic medium, as a durable coating for carbonate stones.

They reported that antimicrobial and hydrophobic features have been induced for the treated samples. As a supplement of these findings, a recent study of Crupi et al. [14] has demonstrated that a mixture of TiO₂ nanoparticles and siloxane-based polymeric material was able to penetrate deeply into the stone matrix and to produce a self-cleaning surface. Moreover, a sustainable protective coating for outdoor stone monuments was tested through another formula based mainly on titanium dioxide-PCU nanocomposite [15].

In a parallel platform, HAp-NPs films have been applied successfully in conservation field as a protective layer against the environmental factors, most probably due to the low solubility of these nanoparticles [16]. It is believed that this mechanism was proposed since HAp is the most stable phase at pH>4 [17]. In their study to protect the surface of some architectural structures, Sassoni et al. [18] have reported that the application of nano-TiO₂ over a previously formed HAp-NPs layer was resulted in durable effective self cleaning properties. As a further matter, excellent mechanical properties are produced by HAp-NPs. Methodologically, stone consolidation with hydroxyapatite (HAp) is based on exposing calcite to an diammonium hydrogen phosphate (DAP) solution. This reaction is strongly affected by the concentration of solution, temperature, pH, and other parameters [19].

Objective of the Study

This research was planned to test the efficiency of hydroxyapatite nanoparticles (HAp-NPs), produced by a wet-chemical process, to achieve a good durability to archaeological lime plasters. The assessment methodology was based mainly on determining the inner matrix morphology, surface microtopography, BET surface area and the physical-mechanical properties of the tested samples.

Methodology

Synthesis of HAp-NPs

The hydroxyapatite nanoparticles used in this study were prepared using a wet chemical process. This synthesizing procedure is depending on using an aqueous solutions at relatively low temperatures. In our case, the HAp-NPs have been produced according to the method of Yubao et al. [20]. In this method, an aqueous solution of diammonium phosphate ((NH₄)₂HPO₄) is added to a solution of calcium nitrate (Ca(NO₃)₂·4H₂O). The mentioned chemicals were supplied from Sigma-Aldrich (assay ≥ 98.0%, reagent grade). Determining the grain size of the formed NPs was available by changing the reaction parameters. The pH value of the reaction was remained at 10 and 12. Then, the solution was stirred at room temperature for 24 hrs. Quite, the wet chemical process allowed forming needle-like shape and small HAp particle size [21, 22]. In previous experiments, the needle-like HAp-NPs were formed at a lower temperature of 40°C [23].

Samples

The plaster samples analyzed in the current work were collected from El-Bagawat cemetery in the El-Kharga Oasis of the Western Desert, Egypt. Historically, the early date of the cemetery goes back to the 4th century AD. Indeed, the aggressive arid conditions of the oasis are inducing a serious damage to the murals. As a result, numerous destructive mechanisms work in multiple levels. Several deterioration aspects such as detached areas, exfoliation, lack of cohesion, cracking and blistering were observed. Five (5) samples from deteriorated plaster layers plus some fragments (with approximately dimensions: 2cm×3.5 cm) were collected from an undecorated wall niche in the chapel No. 25 at the cemetery. Next, the samples were studied analytically to identify their mineralogical and chemical composition. Deriving from these results, laboratory models were prepared for the experimental section.

Preparation of laboratory mortars

Silicon rubber moulds with dimensions of 50×50×50 mm were used to cast the mortar cubes. The specimens of lime mortars were prepared using quicklime -slaked with water addition-, marble dust and washed river sand (in proportion 1:4:0.5, respectively). Another group of mortar samples was produced by adding HAp-NPs (5.0% by weight) to the previous mixture. To ensure a good distribution of the fluids, the mortars were casted in form of layers. After casting was finished, the mortars were kept to dry for 28 days at a temperature of $20 \pm 2^\circ\text{C}$ and a relative humidity of $65\% \pm 5\%$.

Optical microscopy

A “DNT” digital mobile USB microscope was used to examine the samples. This high-tech microscope allows measurements with magnifications of 10x to 500x with an accuracy of 1 μm .

Field-Emission Scanning Electron Microscope (FE-SEM)

Field-emission scanning electron microscope (Model Philips Quanta FEG 250, Holland) with an accelerating voltage of 20 kV was used to analyze the morphological nature of the studied samples. The micro-chemical analysis was delivered through the EDS unit attached to the SEM instrument.

Transmission Electron Microscope (TEM)

The structural characterization, morphology and dispersion of the synthesized HAp-NPs were examined using a JOEL JEM-2100 transmission electron microscope equipped with a Gatan digital camera Erlangshen ES500. The instrument was operated at an efficient voltage of 200 kV.

Atomic Force Microscope (AFM)

The roughness of the samples and their microtopographic profiles were obtained through a high resolution Aligent 5600LS Atomic Force Microscope.

X-ray diffraction analysis (XRD)

X-ray diffraction analysis was used to determine the mineralogical structure for the archaeological samples and the synthesized nanoparticles. The XRD patterns were obtained using a XPERT PRO PANalytical diffractometer which was operated at 45 kV, using a Cu-K α radiation at wavelength of 1.54060 Å. The generator current was kept at 30 mA.

Brunauer-Emmett-Teller (BET) surface area and Pore-Size Analysis

The NOVA-touch pore-size analyzer was used to measure the pore size distribution and BET surface area of the studied samples. Pore size range of the instrument was of 0.35 to 500 nm (3.5 to 5000 Å).

Physical and mechanical testing

The mechanical behavior of samples was determined using a Shimadzu AG-I Mechanical Test Instrument (MTI), which enables an automatic compression testing. The maximum force magnitude was of 15 kN with a test speed of 1 mm/min. The measurements were determined following the RILEM standards [24].

Results and Discussion

Characterization of the plaster samples

By the microscopic examination on a rough fragment, fine lime aggregates with slightly small size and various coarse grains were appeared (Fig. 1, up, left). The fine aggregates suggest that a soft-burnt stone type perhaps was the source of lime [25]. Large siliceous particles were also observed, which occupy a high percentage of the whole matrix (Fig. 1, down, left). The FE-SEM micrographs on the samples showed assemblages of smooth grains together with large grains. What's more, large pores and cavities can be easily observed (Fig. 1, up and down, right).

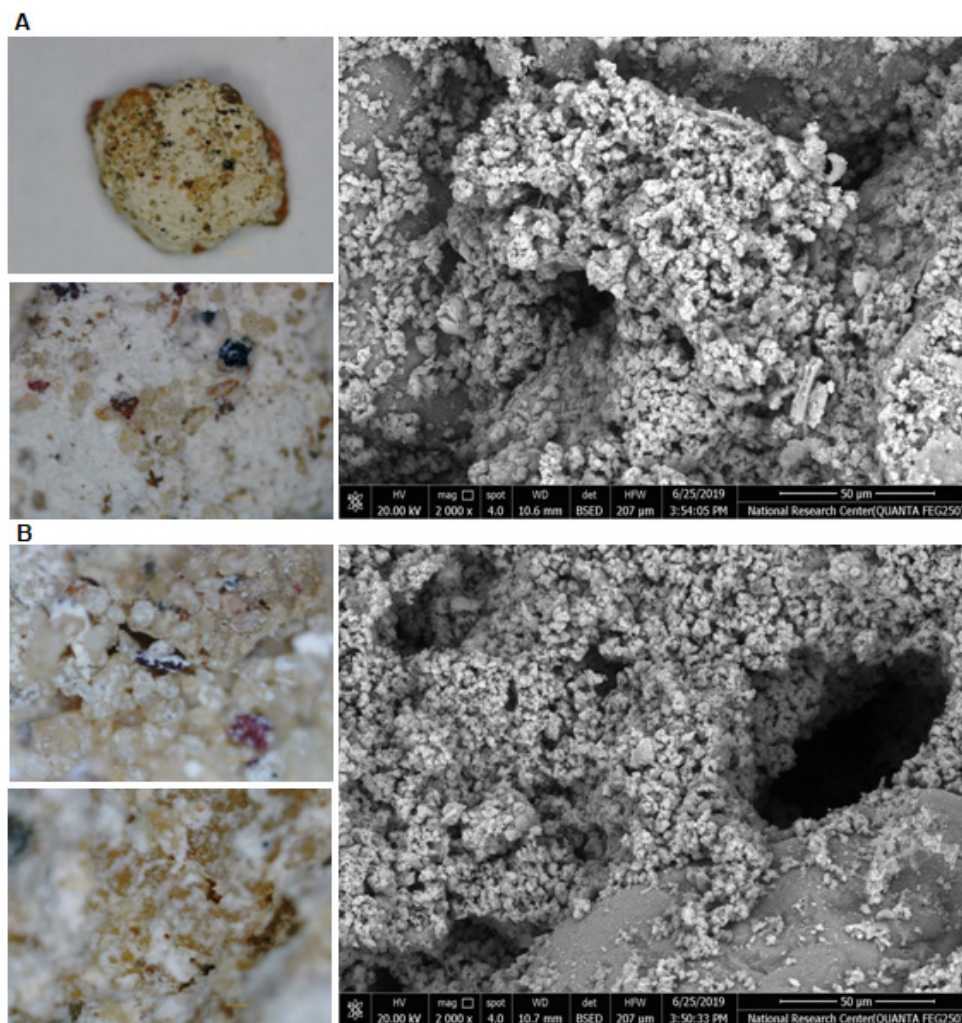


Fig. 1 Optical photomicrographs and FE-SEM micrograph of the plaster samples

An EDX bulk microanalysis on a plaster sample showed high quantities of silica together with calcium, aluminum, potassium, sodium and iron. Figure 2A shows a representative EDS spectrum of the plaster sample. The microanalysis (compound %) of the archaeological plasters, by SEM-EDS, is given in Table 1. XRD analysis revealed crystalline phases of quartz (SiO_2) as the major component in all samples and minor amounts of calcium carbonate (calcite, CaCO_3). Traces of plagioclase (albite, $\text{NaAlSi}_3\text{O}_8$), potassium feldspar (microcline, KAlSi_3O_8) and clay minerals were also reported. Figure 2B shows a representative XRD pattern on the plaster powder samples.

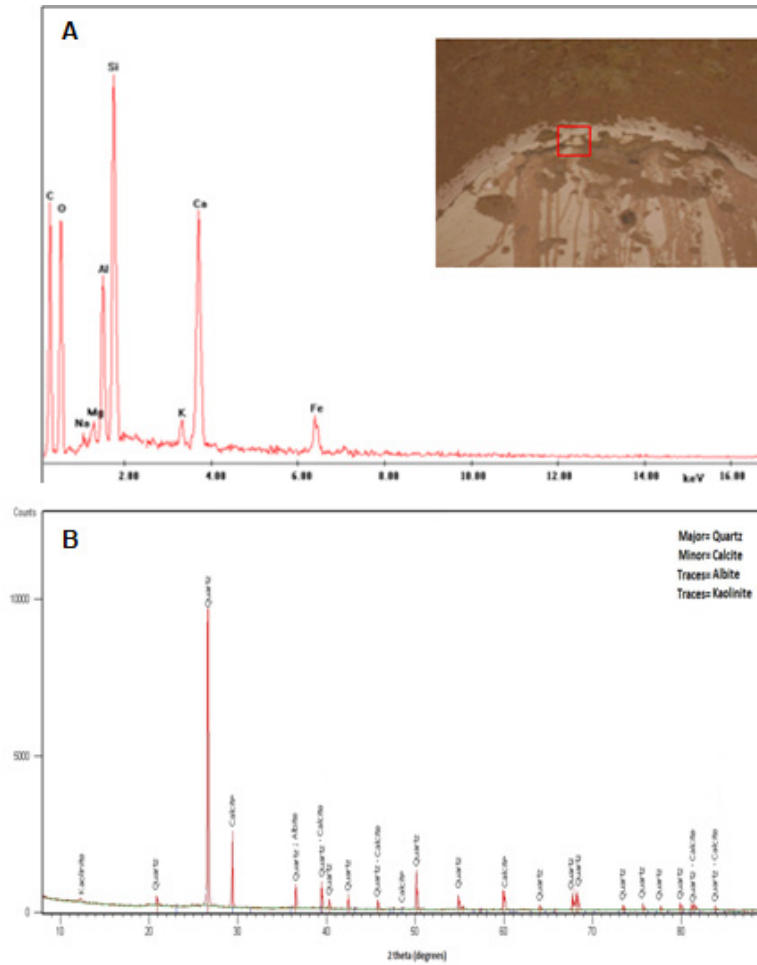


Fig. 2 (A) EDX spectrum recorded on the plaster sample; (B) XRD pattern obtained on the sample

Table 1 SEM-EDS chemical analysis of the archaeological plasters

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
2.66	1.44	12.42	25.50	0.76	53.01	1.07	1.90
2.23	2.33	10.77	30.94	1.26	47.62	1.55	2.57
2.19	1.09	10.04	26.02	0.89	55.88	1.62	2.24
1.99	1.76	10.67	22.65	1.21	57.43	0.98	2.31
2.05	2.11	11.54	25.43	1.77	53.86	1.22	1.98

Characterization of the synthesized HAp-NPs

X-ray diffraction analysis of the synthesized nanoparticles showed familiar diffraction pattern and peaks orientation of hydroxyapatite (basically of JCPDS card no. 09-0432) (Fig. 3, up). Not only this, but also the strong XRD peaks suggest that good crystallized particles have been formed. The morphological study by FE-SEM and TEM showed clearly the needle-shape nanoparticles. The particle size range, measured by FE-SEM, was between 46 and 72 nm (Fig. 3, down).

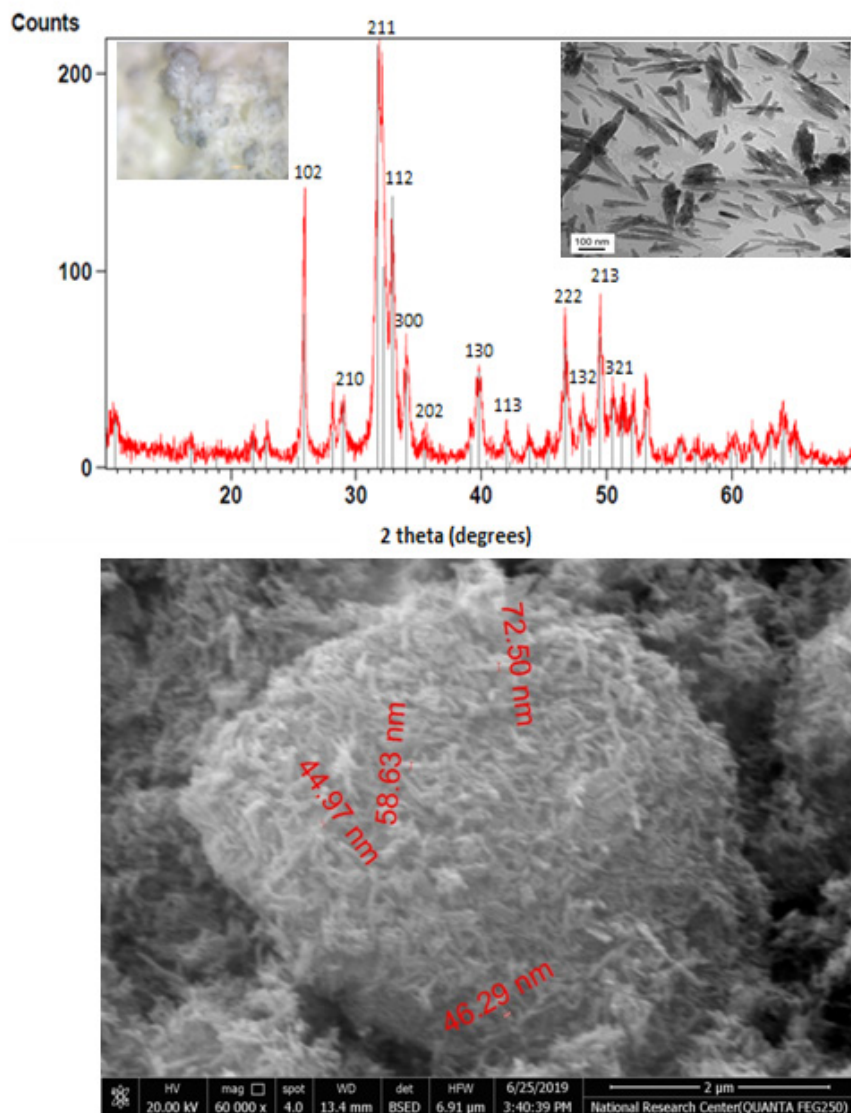


Fig. 3 XRD pattern, TEM and FE-SEM micrographs of the synthesized HAp-NPs

Treating the archaeological plasters with HAp-NPs

Practically, there are many methods for applying the consolidating materials to the substrate as the simple brushing, injection, spray, etc. [26]. The plaster samples were treated for five times by brushing a 10% (w/v) colloidal HAp-NPs dispersion in 2-Propanol. Then, the samples were left in room temperature for 21 days, then, their microscopic-morphological features were determined by OM, FE-SEM and AFM methods. The physical-mechanical features and BET surface area/pore size distribution were evaluated. Fig. 4 shows representatives OM and FE-SEM micrographs captured on the treated samples. The microscopic images showed that the plaster grains which are masked with the white HAp-NPs (Fig. 4A). As well, the observations showed that the inner pores were filled with NPs which produced a notable cohesion, as discussed below in the mechanical merits of samples. The FE-SEM micrograph on a treated sample revealed a fine morphological structure with small pore size. The investigations performed after two weeks from the first application of the suspension (Fig. 4B) showed a dramatic decrease in porosity beside a homogenous flow of the HAp-NPs within the substrate. After the complete curing of the suspension, the deposition of HAp-NPs in deeper zones in the samples was also ascertained (Fig. 4C). A cross-sectional bulk EDX microanalysis performed on a treated sample (Fig. 5) showed the existence of phosphorus together with high calcium concentration. This confirms that a sufficient breakthrough of the NPs into the substrate matrix was acquired. Clearly, this is due to the ability of the nano size of particles to achieve a sufficient permeation and to occupy a high volume of the treated substrate [27]. As good

as, the eminent deposition of HAp-NPs is due to the slightly large surface area and the distinctive low solubility of HAp-NPs. Another significant factor is the lattice constants of HAp-NPs, which match those of calcite [28]. After many presumed restoration principles, it is needful to use restoration materials similar to the original objects in order to achieve a desirable harmonization in the physiochemical-mechanical traits.

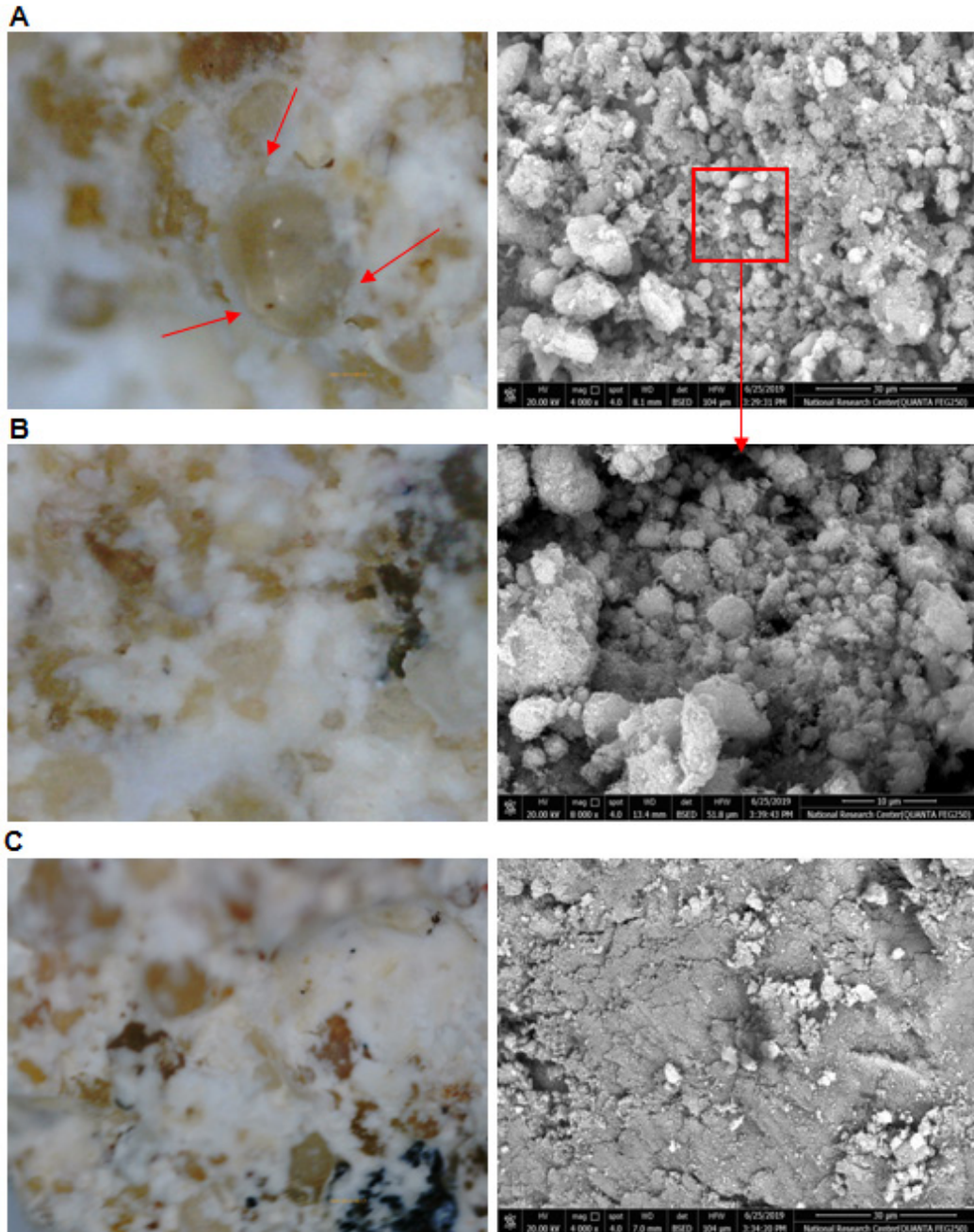


Fig. 4 Optical photomicrographs and FE-SEM micrograph of the treated samples with HAp-NPs (A: after 48 hrs of treatment; B; after 2 weeks, C: after 28 days)

The AFM surface plot profiles recorded on the control samples show diversified large grains (Fig. 6A). For the treated samples, there is a clear disparity through the microtopographical features that the NPs are distributed uniformly. The treated models showed an average height difference of 6.41 nm, which reflects a significant increase of the roughness (Fig. 6B). This achieved a better bonding to the inner matrix. In the same way, the uniform spreading of HAp-NPs has influenced the surface area resulting in an expansion by a 26% for the BET surface area and decreasing the pore size by an average of 40%.

By testing the laboratory samples mechanically, the compressive strength showed values of 6.3 MPa before treating the samples to 9.4 MPa after processing, which provided an excess in the material bearing of 30%. The physical properties measured on the treated cubes confirmed high values of density and real density. The water absorption and porosity have been reduced which indicate that the pores were filled with NPs. A series of previous and recent studies has shown that nanoparticles can enhance reproducibly the physical and mechanical features of different types of stones, mortars and plasters. Several effects can be observed in form of considerable shortage of the capillary water uptake, creating multi-aspects roughness profiles and increasing the compression strength/surface cohesion plus creating protective coatings against the weathering factors [29-31].

Table 2 summarizes the physical-mechanical features and BET surface area/pore size analysis of the laboratory samples before and after cycles of salt weathering.

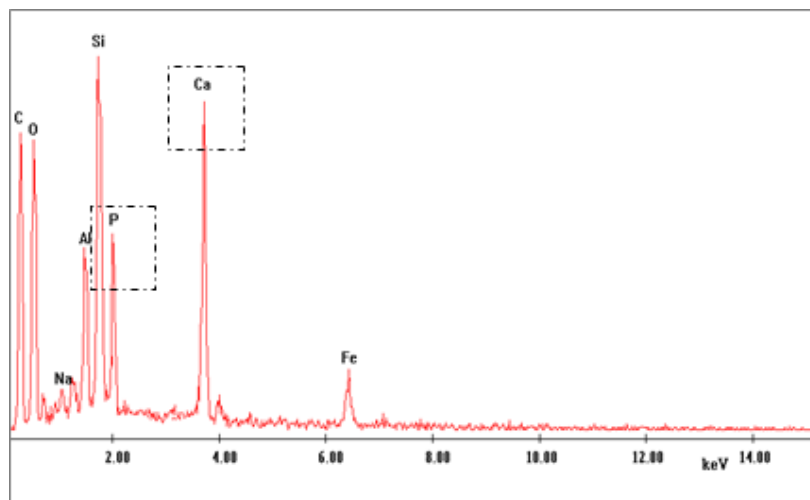


Fig. 5 EDS spectrum obtained on a cross-section of the treated plaster

Table 2 Physical- mechanical and surface properties of laboratory models

Property	P1	P2	P1*	P2*
Density, g/cm ³	1.3	1.6	1.1	1.4
Real density, g/cm ³	2.6	2.9	2.3	2.7
Water absorption, %	23	21	28	24
Porosity, %	39	32	43	36
Compressive strength, MPa	6.3	9.4	5.5	7.9
BET Surface area, m ² /g	23.2894	26.774	20.0876	24.1265
Average Pore Size, nm	2.6287	2.2765	2.34125	2.1542
P1= without HAp-NPs		P1*= without HAp-NPs after salt weathering		
P2= with HAp-NPs		P2*= with HAp-NPs after salt weathering		

Sufficiently, the treatment made the plaster samples more compact and less permeable to water [32]. Otherwise for stone monuments, salt weathering is considered an aggressive deterioration factor. For this, the stability of samples against laboratory cycles of salt weathering were evaluated. In this test, the samples were immersed in a solution of 2-4% sodium chloride, NaCl (weight salt/weight dry specimen) for 4 hrs and then they were heated in an oven for 8 hrs at temperature of 105 °C. Thereafter, the samples were placed in the room temperature for 4 hrs. The described procedure was repeated for 17 times. In prospect, the control models showed a serious damage and a partial failure was occurred after two cycles only of the weathering. The treated samples showed a convenient stability compared to the control ones. The AFM images recorded on the control mortar cubes after salt weathering showed a slight increase in pore size (Fig. 7A) compared to the treated

ones (Fig. 7B). The roughness profile section height difference of control and treated samples was between 0.863 and 0.750 nm, respectively.

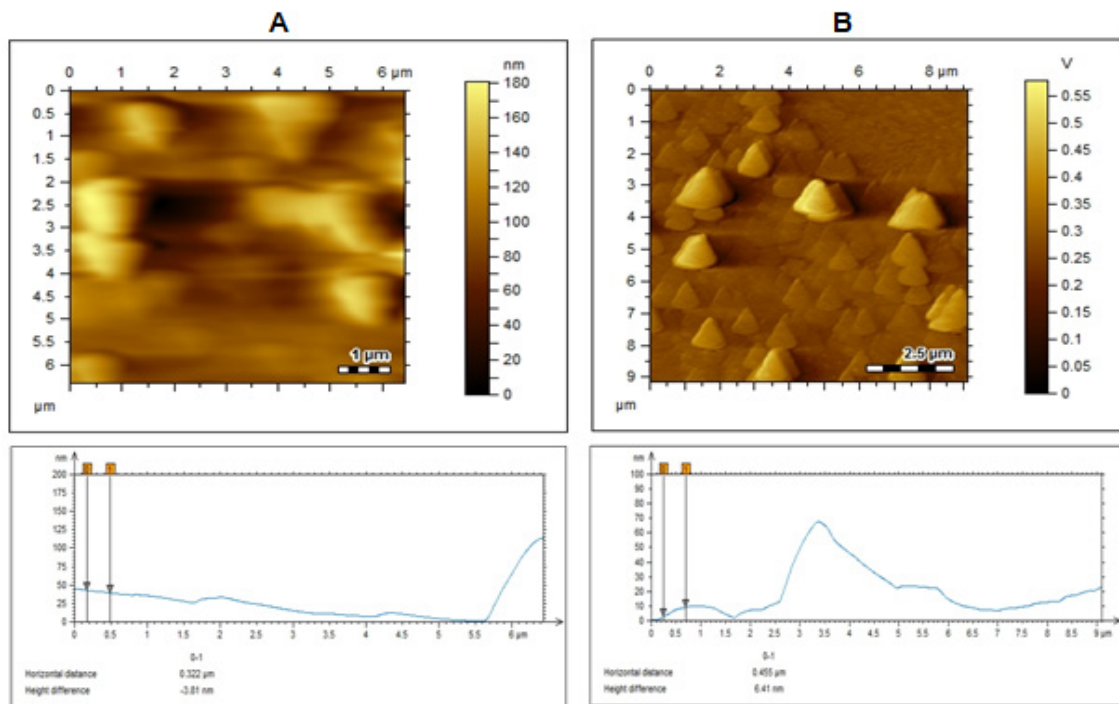


Fig. 6 AFM plot surface and microscopic profiles of control (A) and treated samples (B)

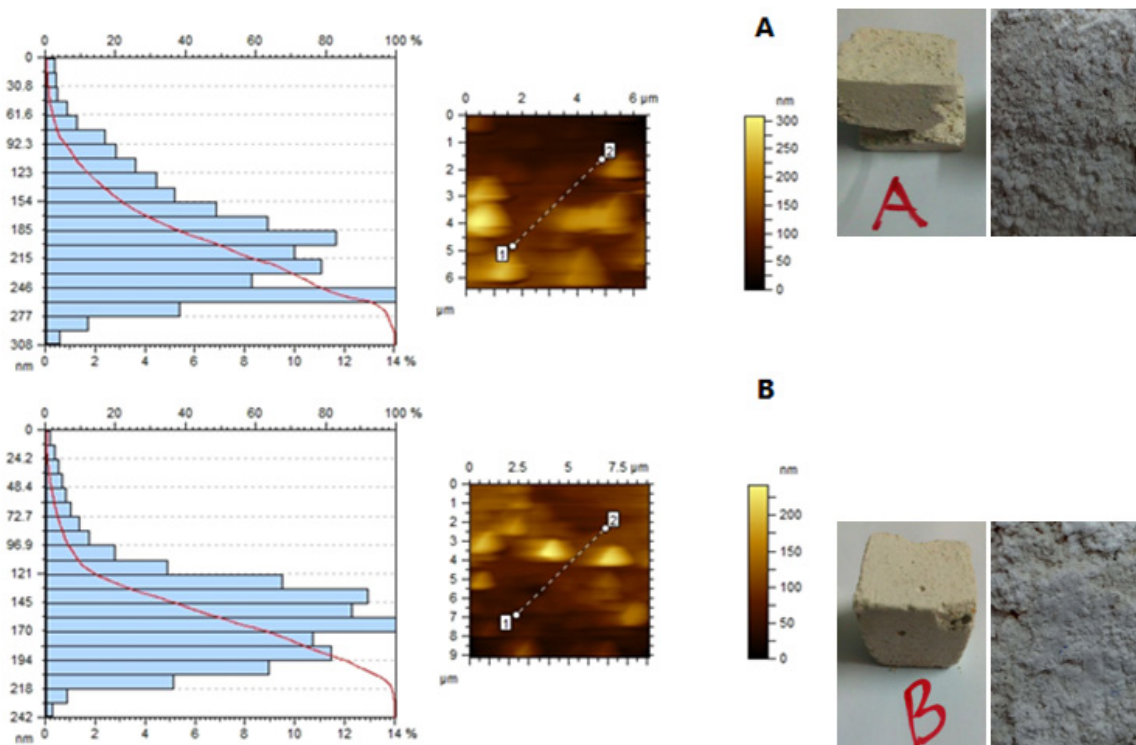


Fig. 7 AFM images of the treated and control samples after salt weathering

Conclusions

This study was pointed to evaluate the efficiency of wet chemical-synthesized HAp-nanoparticles for a compatible restoration of archaeological lime-based plasters. The strength-durability of the treated samples was tested via numerous analytical methods. In addition, the physical and mechanical properties were evaluated. The microscopic-morphological observations, surface

microtopography by AFM, BET surface area/pore size analysis were constructive to record the modifications of the treated substrates. The results showed that the HAp-nanoparticles achieved a good cohesion to the inner matrix through physical-mechanical improvements.

The uniform distribution of HAp-nanoparticles within the inner matrix has enhanced, positively, the roughness profile of the treated samples. Moreover, remarkable compressive strength values were achieved. A desirable reduction in water absorption and porosity of the treated samples was also notified. Certainly, the low solubility of HAp-nanoparticles can be calculated as a key factor for its effectiveness as a restoration material. Lastly, HAp-nanoparticles can be applied distinctively for treating weathered plasters and to improve their long-term durability. As well as, they can be used as additives for the restoration mortar formulas for completing the missing parts in the plaster layers.

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