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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 monumentdegradation. Calcite (the variety of calcium carbonate detected) dissolution is affected by the presence of foreign compounds, 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. Also, vaterite, an unstable rock, contributes to chalk degradation, absorbing negatively charged species (the anion SO_4^{2-} 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 cm^3) 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 ($1.7\ g \cdot l^{-1}$) 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 hydroxyde 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 Chuck 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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(ξ), were used in order to identify the major constituents of chalk stone (metals, anions, type of calcium carbonate), the influence of environmental salts ($MgSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 6H_2O$, $Na_2SO_4 \cdot 10H_2O$ 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 $Ca(OH)_2$ or $Mg(OH)_2$, smaller values were obtained, due to the aggregation tendency of $Ca(OH)_2$ or $Mg(OH)_2$, 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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7. References

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