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Optimizing the In Situ Deposition of Carbonate Hydroxyapatite for the Consolidation of Marble in Cultural Heritage Monuments

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I. EXTENDED ABSTRACT

Strengthening the structure of marble is key to restoring its mechanical properties and contributing to the stability of stone monuments. Marble consolidation as a conservation technique has been attempted since the 1950's, initially using organic consolidants, i.e., acrylics, vinyl and silicone polymers, as well as epoxies [1,2]. These strategies, however, suffered from incompatibility, reversibility and low durability problems and were gradually replaced by the use of inorganic salts or bases with low water solubility. In recent years, the use of calcium hydroxide [3], calcium oxalate [4,5], and hydroxyapatite [6–8] has gained attention for the strengthening and stabilization of deteriorated or fragile marble surfaces. This method generally requires optimized deposition of the above materials in sub-micron or nano-sized particulate form, thus enabling their incorporation into the porous structure of marble, allowing (permitting) an efficient consolidation [9,10]

Hydroxyapatite (HAP), a calcium phosphate with the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is known for its extremely low solubility ($K_{sp} \sim 10^{-98}$); in particular, its carbonate form, carbonate hydroxyapatite (c-HAP), $\text{Ca}_{10}(\text{PO}_4)_{6-y}(\text{CO}_3)_y[(\text{CO}_3)_{x+(1/2)y}(\text{OH})_{2-2x}]$ is commonly found in bones and teeth of vertebrates. The apatite family has been explored for various applications, including its potential for the conservation of marble and other calcareous materials. Marble, a calcareous metamorphic rock, is susceptible to deterioration over time due to environmental factors such as acid rain, pollutants, and biological activity.

The method entails depositing (involves the deposition of) the highly insoluble hydroxyapatite salt from aqueous solutions of diammonium phosphate (DAP). This is achieved by the interaction of diammonium phosphate (DAP) aqueous solutions on the surfaces of calcareous or marble objects of cultural heritage, providing a mechanism to reconnect and restore the cohesion lost in the porous marble substrate. Concurrently, the formation of a thin, sufficiently bonded layer on the surface acts protectively, retarding the decay process. This study evaluated the method's effectiveness combining infrared spectroscopy with SEM-EDX micro-analysis. The method was optimized by the addition of simulated body fluid (SBF), a cocktail of inorganic salts, showing particularly positive results in both immersion and surface application scenarios. Among the application methods tested, the dripping method presented satisfactory results on the monument, although immersion, if feasible, is considered ideal as the most efficient c-HAP formation was observed.

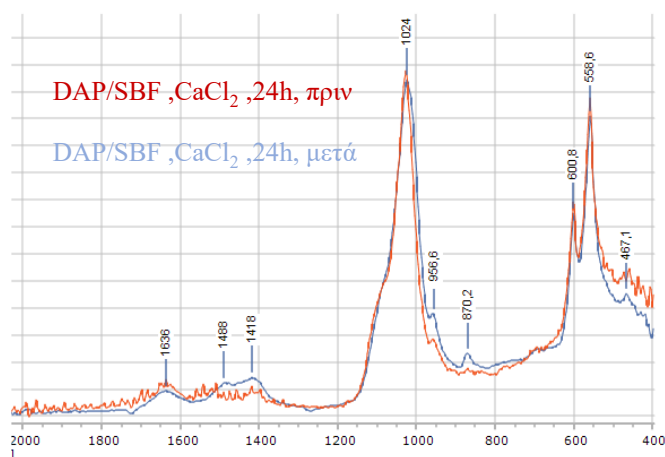


Figure 1. FTIR spectrum of the CaCl_2 -enriched marble area after treatment with DAP, and SBF showing the formation of c-HAP

The HAP formation process requires the availability of calcium through the reaction of DAP with Ca ions, readily provided by the marble itself. This raises the concern of sacrificing some of the marble surface integrity for the consolidation process. At a first level, the formation of c-HAP, as shown by FTIR spectra (Figure 1), demonstrates that some of the calcium provided by the marble still remains in the calcite form. An attempt was also made to further reduce this effect, by enriching the marble surface with CaCl_2 before applying the DAP solution.

The results of the method were highly encouraging, achieving significant hydroxyapatite formation and surface coverage along with satisfactory penetration and adhesion to the surface. Analysis of the FTIR spectra of the reaction products provided insights into the different phases of formation, shedding light on the chemical kinetics and the precise products being formed.

Although additional research is required, this method has shown great promise in terms of strengthening and stabilizing structures, offering compatibility due to its inorganic nature, and potentially providing long-term protection.

REFERENCES

- [1] Miculescu F, Mocanu AC, Maidaniuc A, Dascălu CA, Miculescu M, Voicu Ștefan I, et al. Biomimetic Calcium Phosphates Derived from Marine and Land Bioresources. In: Thirumalai J, editor. Hydroxyapatite - Advances in Composite Nanomaterials, Biomedical Applications and Its Technological Facets [Internet]. InTech; 2018 [cited 2023 Feb 16].
- [2] Doehne EF, Price CA. Stone conservation: an overview of current research. 2nd ed. Los Angeles, Calif: Getty Conservation Institute; 2010. 158 p.
- [3] Kroftová K, Škoda D, Witzany J, Čejka T. Consolidation Of Natural Stone With Calcium Hydroxide Nanosuspension In Ethanol And Verification Of Surface Hardening Rate. In Seville, Spain; 2019 [cited 2024 Mar 15]. p. 359–67.
- [4] Maiore L, Aragoni MC, Carcangiu G, Cocco O, Isaia F, Lippolis V, et al. Synthesis, characterization and DFT-modeling of novel agents for the protection and restoration of historical calcareous stone substrates. J Colloid Interface Sci [Internet]. 2015 Jun [cited 2023 Sep 10];448:320–30. Available from: <https://linkinghub.elsevier.com/retrieve/pii/S0021979715001708>
- [5] Ruiz-Agudo E, Álvarez-Lloret P, Putnis CV, Rodríguez-Navarro AB, Putnis A. Influence of chemical and structural factors on the calcite–calcium oxalate transformation. CrystEngComm [Internet]. 2013 [cited 2023 Sep 11];15(46):9968.
- [6] Sassoni E. Hydroxyapatite and Other Calcium Phosphates for the Conservation of Cultural Heritage: A Review. Materials [Internet]. 2018 Apr 4 [cited 2021 Dec 31];11(4):557.
- [7] Graziani G, Sassoni E, Franzoni E, Scherer GW. Hydroxyapatite coatings for marble protection: Optimization of calcite covering and acid resistance. Appl Surf Sci [Internet]. 2016 Apr [cited 2021 Dec 31]; 368:241–57.
- [8] Ma X. In situ Synthesis and Characterizations of Bio-ceramic Based Hydroxyapatite in the Re-mineralization of Calcium-rich Matrices [Internet]. UCLA; 2017.
- [9] Pesce C, Moretto LM, Orsega EF, Pesce GL, Corradi M, Weber J. Effectiveness and Compatibility of a Novel Sustainable Method for Stone Consolidation Based on Di-Ammonium Phosphate and Calcium-Based Nanomaterials. Materials [Internet]. 2019 Sep 18 [cited 2023 Feb 16];12(18):3025.

[10] Capitelli F, Dida B, Ventura GD, Baldassarre F, Capelli D, Senesi GS, et al. 2 Functional nano-hydroxyapatite for applications in 3 Conservation of Stony Monuments of Cultural Heritage. 2020 Nov;11.

