

DOI: 10.5281/zenodo.7977919

SURFACE TREATMENTS USING NANOPARTICLES AND PHYSICOCHEMICAL METHODS FOR THE PROTECTION OF ANCIENT MONUMENTS BUILT OF CALCITIC MATERIALS

Efstathia I. Pavlaku^{1,3}, Christine Lemonia¹, Emily Zouvani¹,
Christakis A. Paraskeva^{1,3}, Petros G. Koutsoukos^{*2,3}

¹University of Patras, Department of Chemical Engineering, Laboratory of Transport Phenomena
and Physicochemical Hydrodynamics, Patras, Greece

²University of Patras, Department of Chemical Engineering, Laboratory of Inorganic and Analytical
Chemistry, Patras, Greece

³FORTH/ICE-HT, Institute of Chemical Engineering Sciences, Patras, Greece

Received: 01/03/2023

Accepted: 27/05/2023

Petros G. Koutsoukos (pgk@chemeng.upatras.gr)

ABSTRACT

Building materials like marble, calcareous stone and mortars rich in calcitic content have been extensively used in ancient monuments. Stone conservation efficiency may be improved considering the mechanisms underlying deterioration due to wet precipitation. In the present work we have tested the possibility of treating calcitic materials with suspensions of amorphous calcium carbonate (am-CaCO₃, ACC) and amorphous silica (am-SiO₂) nanoparticles (NPs). Pentelic marble (PM) in powdered form, to maximize surface area and a mortar from the ancient Roman stadium of Patras consisting of calcium carbonate and silica served as test materials for the validation of the application of suspensions of NPs for protection towards the erosion in slightly acidic solutions undersaturated with respect to calcite (pH 6.50). All solids were characterized by physicochemical methods including X-ray diffraction (XRD), infrared spectroscopy (FTIR) and measurements of BET specific surface area and porosity by nitrogen absorption. ACC nanoparticles, with sizes 200-500 nm were prepared by the development of high saturation through the hydrolysis of dimethyl carbonate (DMC) in alkaline environment of calcium chloride solutions. am-SiO₂ nanoparticles, with sizes between 15-25 nm were prepared by the hydrolysis of tetra ethyl orthosilicate (TEOS). ACC nanoparticles suspensions were rather stable over at least 9 days at room temperature and for over one month at -20°C. am-SiO₂ suspensions were stable for at least 6 months. ACC and am-SiO₂ were deposited on the surface of the test specimens suspended in the synthesis solutions of each of the NP types. The rates of dissolution of the treated specimens decreased significantly. The effect was attributed to the chemical and structural affinity of the NP preparations with the treated building materials.

KEYWORDS: calcitic building materials, amorphous calcium carbonate, amorphous silica, Pentelic marble, mortar, treatment, dissolution rates, nanoparticles, FTIR, XRD

1. INTRODUCTION

Marble and limestone have been widely used in building materials of historical monuments, mainly in the Mediterranean basin and in southern Europe. The masonry of historic buildings was stabilized by the use of mortars, consisting of silica and calcite formed by carbonation of $\text{Ca}(\text{OH})_2$ (Syrmakezis, 2006). The main component of marble and limestone and important constituent of mortars is calcite, which makes them prone to chemical dissolution because of the wet precipitation. The problem is intensified at conditions of environmental pollution in which the concentration of acid gases (SO_2 , NO_x) is sufficiently high to make rainwater quite acidic (Spathis *et al.* 2018). Microorganism colonies on the surface of the calcareous materials of monuments contribute to the development of a microenvironment favouring stone erosion. Materials incompatibility during restoration interventions have also caused significant, irreversible damages (Baglioni *et al.* 2013; Sadat-Shojai *et al.* 2009; Abdelraheem, 2020).

The use of preparations of nanoparticles of metal oxides and hydroxides (TiO_2 , ZnO , $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and metal nanoparticles (Au, Ag, Pt)) as consolidants and/or protective additives has been suggested over the past decades (Ion *et al.* 2018; Ion *et al.* 2018; Blee *et al.* 2008; Caner *et al.* 2018). Suspensions of colloidal silica particles have been successfully used in monuments, protecting them from deterioration associated with erosion, and they proved to consolidate degraded stones (Chandra *et al.* 1999). Silica nanoparticles protect calcareous materials penetrating inside pores forming a protective layer following interaction with calcium carbonate component (Storemyr 2001). Treatment of historic mortars and tuff stone with silica nanoparticles, average size 10-15 nm, interacted with calcium carbonate forming xerogels upon water loss and showed satisfactory consolidation (Sierra-Fernandez, 2017; Stuff, 2020; Tesser, *et al.*, 2018). The use of biopolymers and siloxane materials affecting surface properties have shown promising perspectives in the protection of monuments (Helmi, *et al.*, 2022; Manoudis *et al.*, 2017).

Amorphous calcium carbonate (ACC) is the least stable crystal form calcium carbonate. ACC particles in suspension are efficient consolidants for calcareous matrices suggesting high potential for stone treatment to protect it from damage (Wang *et al.*, 2022). ACC particles forming upon contact of nanolime with carbon dioxide have been tested with success as conservation materials (Rodriguez-Navarro, 2016; Baglioni 2021; Burgos-Cara, 2019). The effectiveness of ACC in protecting calcareous materials, beyond the

consolidation action may be due to its compatibility with calcite, the main component of calcareous stone and to its sacrificial dissolution.

In the present work, ACC and silica SiO_2 nanoparticle suspensions were prepared, and subsequently applied on Pentelic marble (ca. 98% calcite content) and on a historical mortar sample, and the protection against erosion from wet precipitation was evaluated from measurements of the rates of dissolution in solutions undersaturated with respect to calcite and acid pH (6.50). The novelty of this investigation is based on the idea that treatment of historic monuments with NPs depends strongly on the interaction of the overlayer with the substrate. We attempted to prove this hypothesis by not simply depositing particles suspended in a medium by simple gravitational deposition, but through affinity interaction with the substrate. Thus, we performed treatment with the substrates introduced in an aqueous medium in which nucleation and crystal growth of the NPs takes place heterogeneously, with the substrates providing the active sites for nucleation and subsequent growth.

2. MATERIALS AND METHODS

2.1. Materials

Powdered Pentelic marble (PM) was used as a model system for CaCO_3 and SiO_2 nanoparticles deposition, to test the effect of application of the synthesized suspensions on the protection from dissolution in acidic media. Two application methods of CaCO_3 nanoparticles on PM were applied. The historical mortar sample was obtained from the Roman stadium in Patras (built between 80-90 AD, probably a gift from the Roman emperor Domitian, Patras, Greece) consisted mainly of calcite and silica, with a ratio SiO_2 : CaCO_3 = 0.67, i.e. 60% calcite content.

The preparation of ACC nanoparticles was done by the addition of 0.05 M dimethyl carbonate (DMC, Merck SA, for synthesis, Taufkirchen, Germany), sodium chloride (NaCl, Merck Greece SA, Athens, Greece) 0.1 M and calcium chloride (CaCl_2 , Riedel de Haen, Seelze, Germany) 0.01M in a 150 mL, magnetically stirred batch reactor at 25.0 °C (concentrations correspond to the final solution prepared) (Faatz M, 2004). Mixing of the solutions lasted 2.5 min before the separation of the precipitate from the solution. The solid was separated from the suspension by centrifugation at 2500 rpm for 4 minutes, then by filtration through membrane filters (0.20 μm , Sartorius, Goettingen, Germany) and it was rinsed with acetone and freeze dried.

Amorphous silica nanoparticles were prepared by the hydrolysis of tetraethyl orthosilicate (TEOS, Sigma Aldrich, Merck, Darmstadt, Germany) (0,29 M)

solution, in ethanol (C_2H_5OH , 95% w/v) and ammonia (NH_3 , 32% w/v). Before the addition of TEOS, the ethanol-ammonia solvent mixture was homogenized by magnetic stirring for 30 minutes, followed by the addition of TEOS. The solution was turned cloudy because of the formation of am-SiO₂. The suspension was stirred for 1 hour from the start of TEOS addition (Singh, 1999). The solid was separated from the suspension by centrifugation at 40,000, rpm for 30 min.

2.2. Methods of Solids Characterization

The prepared and/or treated solids were characterized by physicochemical methods (powder X-ray diffraction, XRD, measurements of specific surface area with nitrogen adsorption according to the Brunauer, Emmet Teller isotherm (BET), Fourier transformed infra-red spectroscopy (FTIR), micro-Raman spectroscopy (mR), and thermogravimetric analysis, (TGA) (TA Instruments, Q50). More specifically, XRD patterns were recorded with a Siemens D-500 machine, using Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm) and operating at 40 kV and 30 mA over the range of 10-70 2 θ ⁰. The powdered samples were placed on the appropriate holders and diffractograms were obtained at a rate of 0.2 2 θ ⁰/s. The specific surface area (SSA) of the specimens was measured by nitrogen absorption (Micromeritics, Gemini II 2375) over a range of ratios of nitrogen pressure, p , over the atmospheric, p_0 , $p/p_0 = 0.10, 0.15, 0.20, 0.25$ and 0.30 . From the nitrogen adsorption-desorption isotherms over the entire range of p/p_0 between 0.05-1, the porosity was calculated (Stardriver II[®] software, micromeritics). The FTIR spectra were recorded over the wavelength range 4000 to 400 cm^{-1} using a FTIR spectrometer (Digilab Excalibur) 20 scans at resolution of 2 cm^{-1} . Raman spectroscopy (Renishaw inVia Reflex Raman microscope) was used for the identification of the calcium carbonate polymorphs. The measurements were carried out using excitation laser line at 785 nm. The Raman system used collected approximately 7×10^5 Raman spectra in the spectral region 100–1200 cm^{-1} . TGA analyses were obtained in nitrogen atmosphere at a heating rate of 5 K/min. The morphology and particle size were examined by scanning electron microscopy (SEM, Zeiss, Leo-Supra 35V) equipped with a microanalysis unit (Bruker).

2.3. Treatment of the test specimens with nanoparticles (NP)

The material to be treated (Powdered PM or the historic mortar sample) with ACC NPs, was suspended in a solution containing DMC and CaCl₂ (concentrations as in 2.1). The suspension was thoroughly mixed by magnetic stirring until homogeneous. Next the appropriate sodium hydroxide solution was

added to make the suspension alkaline and initiate hydrolysis of DMC, which resulted in the precipitation of ACC. Stirring of the alkaline suspension continued for 2.5 min more and the solid was separated from the fluid by filtration through membrane filters (0.1 μm , Sartorius), freeze dried and kept at -20⁰C.

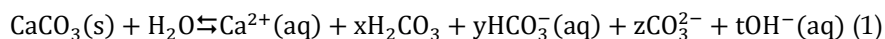
For the treatment with am-SiO₂ NPs the test materials were suspended in ammonia solution in 95% ethanol. Ammonia concentration in the final solution was 0.67M. Following homogenization of the suspension with magnetic stirring, TEOS was added and am-SiO₂ formed immediately. The mixed suspension was allowed under stirring for 30 more minutes and the solid was separated from the liquid phase by filtration. The solid was next dried at 60⁰ C for 24 hours and was kept in a desiccator.

The treatment of the test samples with the composite material ACC-am-SiO₂ was done by the addition of 1.0 g of the test specimens in suspensions of the corresponding particles prepared as described in 2.1 under stirring. The contact time of the test materials with the NPs in the suspension was limited to 10 min. Next, the solid treated test samples were separated from the liquid phase by filtration through membrane filters.

2.4. Dissolution tests. Measurement of the rates of dissolution

The dissolution of the test specimens was studied in undersaturated calcium carbonate solutions at constant pH. The progress of dissolution was assessed measuring the calcium concentration in the undersaturated solutions as a function of time. Solutions undersaturated with respect to calcite (the thermodynamically most stable calcium carbonate polymorph) were prepared in a thermostated batch reactor mixing equal volumes of standard CaCl₂.2H₂O and NaHCO₃ solutions, 75 mL each. Both solutions were prepared from the respective stock solutions, prepared from the corresponding crystalline materials. The calcium chloride stock solutions were standardized with atomic absorption spectrometry (AAS, Perkin Elmer AAnalyst 300) and by titration with standard EDTA solutions with murexide indicator. The sodium bicarbonate stock solutions were prepared fresh in every experiment from the respective crystalline solid (Merck Puriss.) dried overnight at 70⁰C and used without any further standardization. The ionic strength of the solutions was adjusted with sodium chloride from the respective stock solution, made from the solid without any further standardization. In all measurements the total calcium concentration, (C_t), in the undersaturated solutions was equal to the total carbonate concentration (C_t) and equal to 1.25mM. The ionic strength was 0.1M in NaCl. The

pH of the undersaturated solutions was acid (6.50) and it was adjusted by the addition of standard HCl solution (Merck, titrisol). Following the verification of the constancy of the solution pH, 10 mg of the test material was introduced in the undersaturated solutions and it was rapidly dispersed by magnetic stirring.



Where $t=2x+y$. to maintain solution pH, t moles of standard hydrochloric acid should be added to neutralize t moles of OH^- ions released as calcium carbonate of the test materials matrix dissolves. In this type of pH-stat experiments the total carbonate concentration, does not change significantly during dissolution, hence the ratios of carbonate to bicarbonate ions and to the carbonic acid also do not change. The rates of dissolution, can therefore be related with the rate of addition of standard hydrochloric acid solution so that:

$$\frac{\Delta C a_t}{\Delta H^+} = t^{-1} \quad (2)$$

In Equation (2) Ca_t is the total calcium concentration in solution and H^+ the concentration of protons (acid) added to neutralize the OH^- ions released because of the dissolution. Combination of equation (2) with mass and charge balance equations and the equilibria equations allows for the calculation of rates of dissolution (Kazmierczak, 1982). Increase of the solution pH by 0.005 pH units, caused by the dissolution of the carbonate component of the dissolving solid (Equation 1), triggered the addition of standard hydrochloric acid solution from a motorized syringe controlled by a digital computer. During dissolution, samples were withdrawn, filtered through membrane filters and the filtrates were analyzed for (total) calcium by AAS. Analysis for total dissolved silicate was done spectrophotometrically at 350 nm (UV-VIS spectrophotometer Perkin Elmer Lambda) by the construction of the appropriate reference curve of the absorbance of standard samples as a function of their concentration. The analytical method was based on the complexation of silicate ions with ammonium molybdate (Babko, 1976). The initial rates of dissolution

Throughout the dissolution of the calcium carbonate component of the test specimens the pH of the undersaturated solutions was kept constant by the addition of standard hydrochloric acid to neutralize the protons released:

were calculated from equation (2) and were validated from the calcium-time profiles. The rates of dissolution were expressed per unit surface area of the dissolving solid.

3. RESULTS AND DISCUSSION

The characteristics of the test materials treated with the NP preparations are presented in Table 1.

Table 1. Specific surface area (SSA), pore volume (calculated from the BET isotherm) and amount of solid deposited on powdered Pentelic marble and the test mortar.

Material	BET Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)
Powdered Pentelic marble (PM)	8.4	0.029
Mortar	10.0	0.021
CaCO ₃ (ACC)	4.7	0.006
ACC- PM	7.8	0.012
am-SiO ₂	32.5	0.103
am- SiO ₂ - PM	23.7	0.110

As shown in Table 1, the treatment of PM with ACC resulted to the significant reduction of the low pore volume of the material. In the case of am-SiO₂ and because of the predominance of the am-SiO₂ NPs the pore volume of the latter was predominant following the treatment. Apparently, the pore volume measured for the treated PM reflects the corresponding volume of am-SiO₂ which is higher than the respective for PM. The SSA measured in the case of PM treated with ACC dropped significantly while for am-SiO₂ treated sample, the SSA was close to the respective for the NPs of am-SiO₂. The morphology of PM grains and mortar sample are shown in Fig.1.

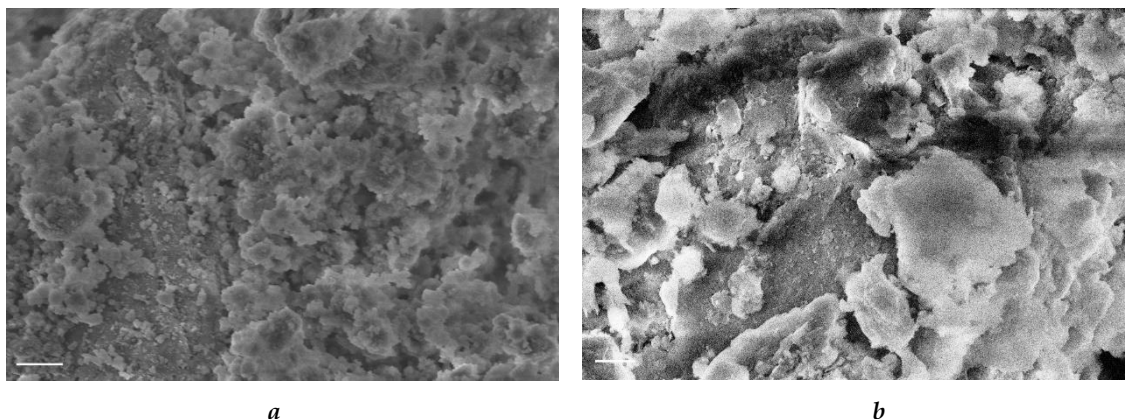


Figure 1. Morphology of (a) Pentelic Marble grains; Bar 1 μm (b) Historic mortar (60% calcite, 40% Silica); Bar 2 μm

As may be seen the powdered Pentelic marble (Fig.1a) consisted of larger calcite grains underlying finely dispersed calcite crystals ($< 1\mu\text{m}$) on its surface. It is anticipated that the small size crystallites dissolve fast leaving the surface unprotected. The content of trace components was very low and was not distinct in the EDS spectra. Moreover, the XRD pattern did

not show any other phase except for calcite. The morphological examination of the mortar sample showed the presence of larger rhombohedral, though not well shaped, calcite crystals covered by silicate crystallites which formed aggregates.

The morphology of the ACC and am-SiO₂ NPs which were used for the treatment of PM and of the mortar are shown in Fig. 2.

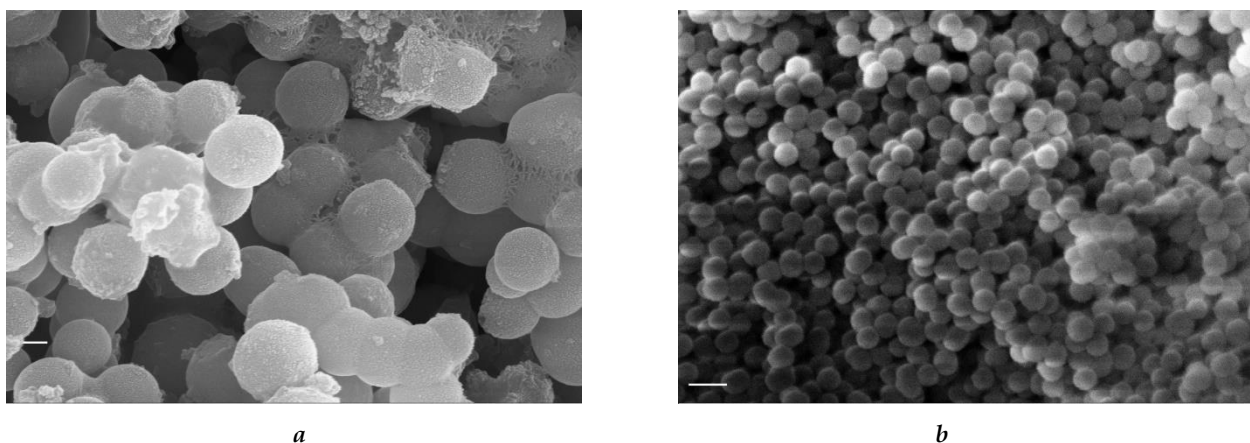


Figure 2. Morphology of NPs for the treatment of calcitic building material: (a) ACC (bar 200 nm) (b) am-SiO₂ (Bar 200 nm)

As may be seen ACC NPs are spherical particles (Fig.1a) with diameters between 200-500 nm while am-SiO₂ NPs (Fig. 1b) were more uniform in terms of size with diameters around 100 nm. The size distribution in this case was more uniform in comparison with the respective of ACC. Examination of the morphological characteristics of the NP preparations in relation with the morphology of the substrates to be treated as shown in Figs. 1a and 1b, suggested that

both, ACC and am-SiO₂ could adhere favourably. Additional factors as chemical and/or structural affinity are expected to yield surface coverage sufficient at least to improve resistance to erosion of the protected materials upon contact with solutions favouring dissolution. The method of preparation of NPs is very important in determining the mean size of silica spheres. The treatment of PM and of the mortar sample resulted to the extensive coverage of the building materials with the NPs as shown in Fig. 3.

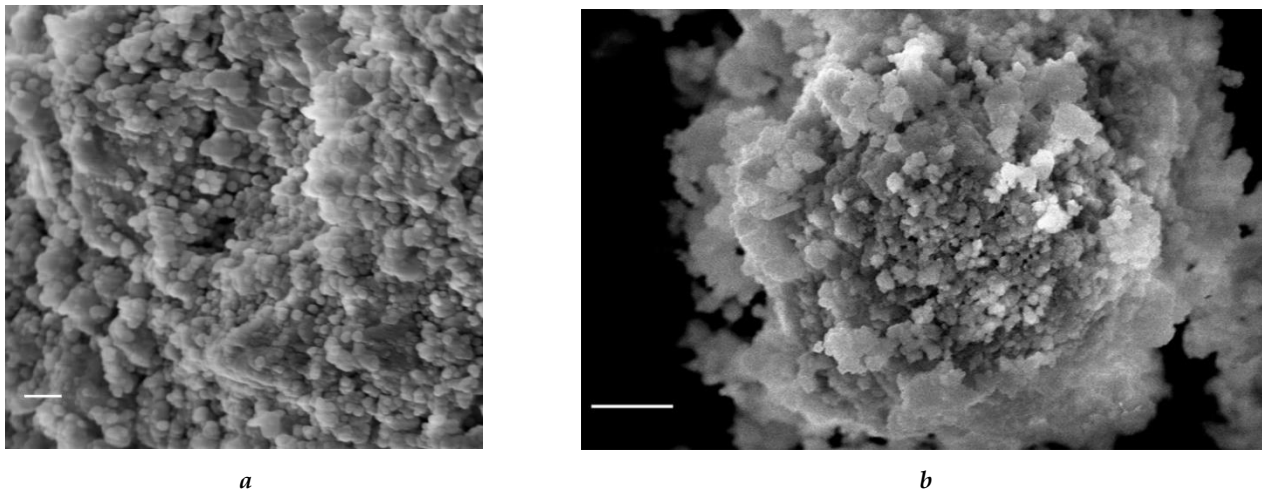


Figure 3. Pentelic Marble grain past treatment with NPs: (a) am-SiO₂ NPs; bar 200 nm (b) ACC NPs; bar 2 μm

As may be seen in Fig. 3a am-SiO₂ particles cover fully the calcitic material in which calcite rhombohedra are covered with the NPs. ACC covered also fully marble grains providing besides consolidation, sacrificial sites of dissolution which can possibly be refreshed by application of the NPs periodically. The full coverage of the test materials with the synthesized NPs when compared with the morphology of the test materials before treatment (Fig. 1) shows that both NPs have the potential of protecting against dissolution. In the case of Fig. 1b, a calcite grain of the

PM is shown (ca. 6 μm diagonal) fully covered by ACC. ACC particles may provide primary sites of (sacrificial) dissolution. Due however to the chemical affinity of ACC to calcite (both are CaCO₃) a stronger relationship is anticipated. The am-SiO₂ nanoparticles seem to be firmly attached onto the calcite crystals of the PM grains and it is anticipated that the layer they form shall prove protective against dissolution.

The morphology of mortar sample, following treatment with ACC and am-SiO₂ NPs respectively, is shown in Fig. 4.

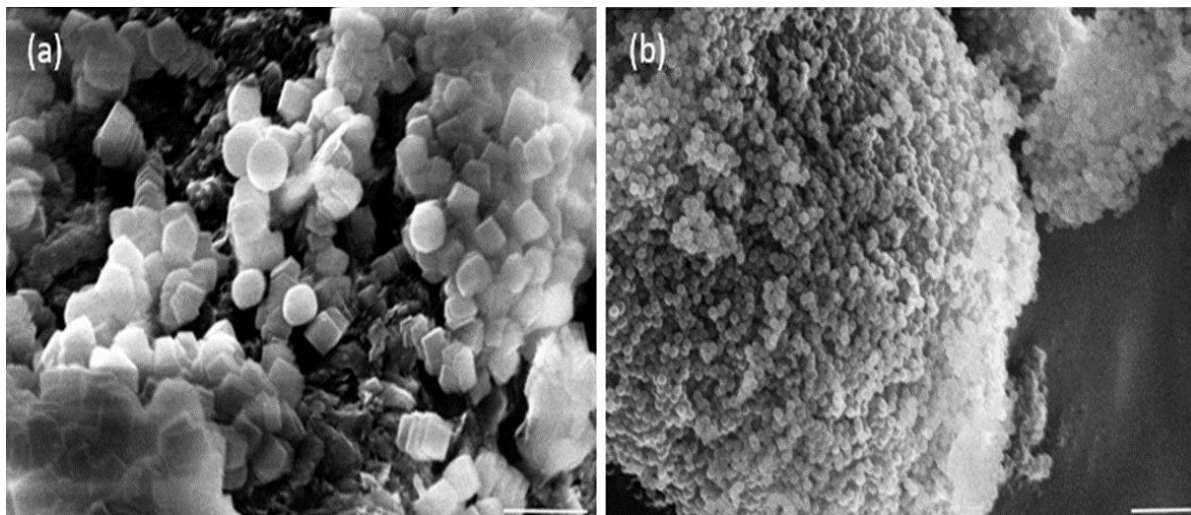


Figure 4. Historic mortar sample (60% calcite, 40% silica) past treatment with NPs: (a) ACC NPs; bar 1 μm (b) am-SiO₂ NPs; bar 1 μm

In Fig. 4a, ACC cover very efficiently the mortar test specimen. As may be seen the ca. 500 nm ACC particles convert gradually to the thermodynamically more stable calcite nanocrystals with the rhombohedral crystal habit. This partial conversion is expected to result to slower kinetics of dissolution. On the other hand, the excellent surface coverage of the mortar specimen with tightly adhering am-SiO₂, as shown in

Fig. 4b, is expected to provide protection of the material against dissolution.

All materials containing calcium carbonate, dissolve in solutions undersaturated with respect to calcite, the thermodynamically most stable calcium carbonate polymorphs. The saturation of calcium carbonate solution with respect to calcite, S_{calcite} , is given by Equation (3):

$$S_{\text{calcite}} = \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_{s,\text{calcite}}^0} = \frac{(\text{IAP})_{\text{calcite}}}{K_s^0} \quad (3)$$

In Equation 3, () denote the activities of the respective ions, their product being the ion activity product, IAP, and $K_{s,\text{calcite}}^0$ is the thermodynamic solubility product of calcite. For $S_{\text{calcite}}=1$ the solution is saturated with respect to calcite and for $S_{\text{calcite}} < 1$ it is undersaturated. The relative undersaturation with respect to calcite is defined as:

$$\sigma_{\text{calcite}} = 1 - S_{\text{calcite}}^{1/2} \quad (4)$$

The rate of dissolution, R_{diss} , of any calcitic material depends on the solution undersaturation:

$$R_{\text{diss}} = k_{\text{diss}} \sigma_{\text{calcite}}^n \quad (5)$$

In Equation (5) k_{diss} is the apparent rate constant of dissolution and n the apparent order of the process. In this work, the results reported refer to $\sigma_{\text{calcite}} = 0.89$.

According to Equation (4), the relative undersaturation is $0 < \sigma_{\text{calcite}} < 1$. The dissolution of mortar sample in solutions undersaturated with respect to calcium carbonate resulted in the increase of the calcium concentration in the undersaturated solutions as a function of time. At the initial stages the rate of calcium concentration change was rapid, slowing down with increasing calcium concentration in the solutions due to the dissolution of the carbonate content of the mortars. This, results to decreasing relative undersaturation ($\sigma_{\text{calcite}} \rightarrow 0$) and to lower rates of dissolution. The concentration - time profiles for the calcium concentration in the undersaturated solutions for untreated and PM treated with suspensions of ACC and am-SiO₂ are shown in Fig.5. The respective profiles for the sample mortar with and without treatment are presented in Fig. 6.

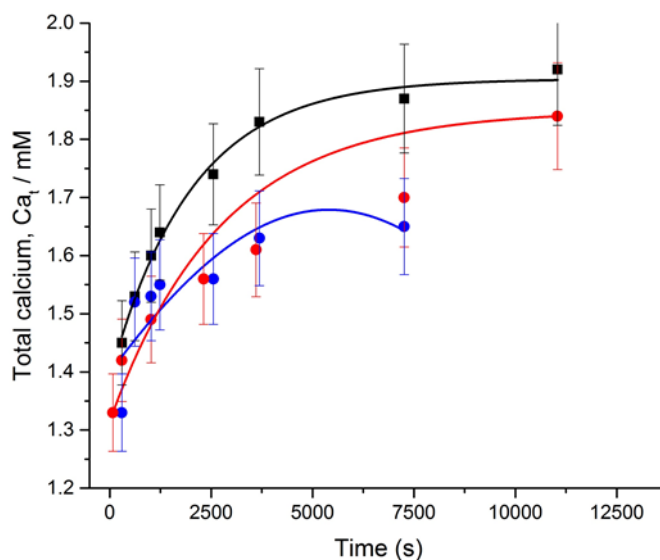


Figure 5. Dissolution of PM in solutions undersaturated with respect to calcite at constant pH; pH = 6.50, $\sigma_{\text{calcite}}=0.89$, 25.0°C. 0.15M NaCl; (■) PM powder; (●) PM treated with ACC; (●) PM treated with am-SiO₂.

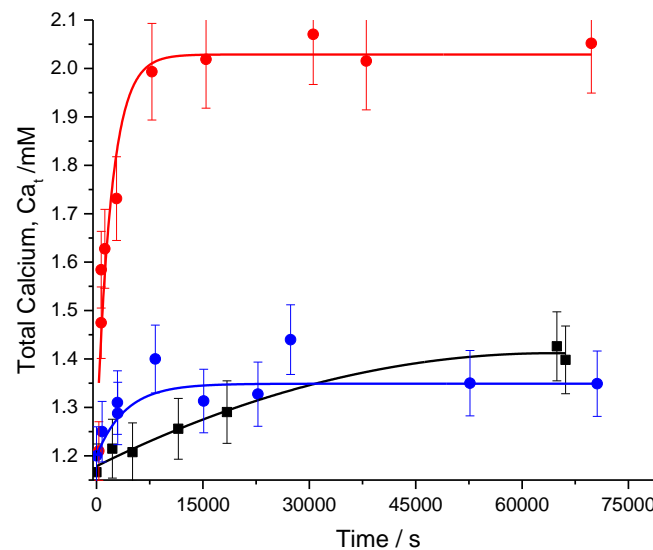


Figure 6. Dissolution of mortar sample, (M) in solutions undersaturated with respect to calcite at constant pH; pH = 6.50, $\sigma_{\text{calcite}}=0.89$, 25.00C. 0.15M NaCl; (■) M powder; (●) M treated with ACC; (●) M treated with am-SiO₂.

The solid lines in Figs. 5 and 6 were obtained by fitting the data with the appropriate function to obtain satisfactory correlation coefficients. The dissolution rates of the test specimens (PM and M) both untreated and treated with the methods described, were calculated as initial rates according to Equation (6):

$$R_{\text{diss}} = \left. \frac{d[\text{Ca}_t]}{dt} \right|_{t \rightarrow 0} \quad (6)$$

The values calculated for the rate of dissolution for all mortar samples without and after treatment with the nanoparticles described are summarized in Table 2. They are reported as moles of CaCO₃ per unit time and per unit surface area of the dissolving material. It was considered that the dissolution takes place stoichiometrically as in equation 1 (Phipps et al. 2001).

Table 2. Dissolution of calcitic materials (Pentelic marble, PM, and mortar sample, M, consisting of 60% calcite- 40% SiO₂) in calcium carbonate solutions undersaturated with respect to calcite ($\sigma_{\text{calcite}}=0.89$); pH 6.50, 0.15M NaCl, 25°C. Rates of dissolution, calculated from the respective calcium- time profiles.

Specimen	Rate of dissolution/ $\times 10^{-8}$ mol · m ⁻² · s ⁻¹
PM	1.40
ACC	3.40
PM treated with ACC	1.30
PM treated with am-SiO ₂	0.30
M	0.40
M treated with ACC	0.30
M treated with am-SiO ₂	0.05

As anticipated ACC yielded three times higher dissolution rates in comparison to the PM which consists

mainly of calcite. However, when PM was treated with ACC the rate of dissolution was significantly lower in comparison with the respective for ACC and even slightly lower in comparison with the rate of dissolution of PM. These results suggested the presence of strong interaction between the calcitic building material with ACC apparently because of their chemical compatibility, which were also reflected in the reduction of pore volume and specific surface area (Table 1). It is clear that ACC particles are protective for PM and the excellent chemical compatibility offers not only sealing of the material but also the replacement of material loss due to weathering. The treatment of PM with am-SiO₂ resulted to rate of dissolution one order of magnitude lower than the corresponding to PM. The am-SiO₂ NPs, with the treatment methodology applied, covered completely the PM grains and as a result it appeared that the porosity of PM was not affected, as the treated material yielded the same porosity as am-SiO₂ NPs. However, the treatment showed excellent protection against erosion upon contact with aggressive aqueous solutions. The structural compatibility of calcite with silica (Lioliou et al. 2007) is an additional advantage contributing to the composite material integrity.

The untreated M sample yielded rate of dissolution ca. three times lower than the respective for PM. It should be considered however that during dissolution, the dissolution of the calcitic component is considered which is 60% (w/w) of the total. Normalization would reduce the difference. In this case the treatment with ACC yielded a small reduction in the

rate of dissolution, which is important for the performance of ACC as weathering inhibitor especially if the high rates of dissolution corresponding to the ACC alone are considered. ACC apparently interacts strongly with the calcitic component of M and protects the specimen from dissolution upon contact with acidic undersaturated solutions. More impressive however was the performance of the treatment of mortar M, with am-SiO₂. In this case, the rate of dissolution was extremely low, one order of magnitude below the respective value for untreated M. The significant content of M in silica favoured the interaction of the specimen with the NPs.

In all cases, the magnitude of the rates of dissolution of both the untreated and of the treated materials suggested, in agreement with results reported earlier for PM (Kanellopoulou et al. 2019) the mechanism of dissolution is controlled by surface diffusion, while the contribution of mass transport is not significant (Fan X. et al. 2022). The mechanism of dissolution, suggested therefore that surface is important for the deterioration of calcitic building materials and elements upon contact with aggressive aqueous media, and that the treatment of PM and M with NPs with suitable characteristics in terms of chemical compatibility and particle size provides effective protection. This protection is best achieved when the surfaces are treated with solutions which ensure direct spontaneous formation of the NPs.

Author Contributions: The authors of this paper Efstathia Pavlaku (EP), Christine Lemonia (CL), Emily Zouvani (EZ), Christakis A. Paraskeva (CAP), Petros G. Koutsoukos (PGK) have all contributed to this publication. EP, CL and EZ have done equally work on the investigation, methodology, analysis, data collection, data curation, writing research work reports. EP wrote the first draft of the paper. CAP and PGK were responsible for the conceptualization, review of the data, securing funding and the administration of the project. All authors have read and agreed to the published version of the manuscript.

ACKNOWLEDGEMENTS

Part of this work was carried out as part of the research projects POLITEIA II, No.MLS 5002478 and by the Stavros Niarchos Foundation within the framework of the project ARCHERS

REFERENCES

- Abdelraheem A. (2020) Investigation of marble deterioration and development of a classification system for condition assessment using non-destructive ultrasonic technique *Mediterranean Archaeology and Archaeometry* Vol. 20, pp. 75-89.
- Babko A.K., Pilipenko, A.T. (1976) *Photometric Analysis: methods of determining non-metals*, Moscow, Mir.
- Baglioni M, Poggi G, Chelazzi D, Baglioni P. (2021) Advanced Materials in Cultural Heritage Conservation, *Molecules*, Vol. 26, pp. 3967-3974.
- Baglioni, P., Chelazzi, D., Giorgi, R., Poggi, G.(2013) Colloid and Materials Science for the Conservation of Cultural Heritage: Cleaning, Consolidation, and Deacidification. *Langmuir*, Vol.29, pp. 5110-5122.
- Blee, A., Matisons, J. (2008) Nanoparticles and the conservation of cultural heritage. *Mater. Forum* Vol. 32, pp. 121-128.
- Burgos-Cara, A., Rodríguez-Navarro, C., Ortega-Huertas, M., Ruiz-Agudo, E. (2019) Bioinspired Alkoxysilane Conservation Treatments for Building Materials Based on Amorphous Calcium Carbonate and Oxalate Nanoparticles, *ACS Appl. Nano Mater.*, Vol. 2, pp. 4954-4967.

4. CONCLUSIONS

Two types of nanoparticles (NPs) were prepared for the treatment of building materials or components consisting of calcite as a major component. Amorphous calcium carbonate (ACC) was prepared by the controlled hydrolysis of dimethyl carbonate (DMC) in the presence of sufficiently high calcium concentrations. The nanoparticles obtained were spherical with particle sizes between 200-500 nm. The particles were stable at low temperature for at least one month. Amorphous silica (am-SiO₂) NPs were prepared by hydrolysis of tetra ortho silicate (TEOS) in ethanol and ammonia. The suspensions obtained were stable and for over 8 months the particle size was in the range between 10-30 nm. Powdered Pentelic marble and a historic mortar from the Roman Patras arena were suspended in the solutions in which ACC and am-SiO₂ were prepared, before the onset of the respective hydrolysis processes. Upon completion of hydrolysis significant coverage of the treated specimens was achieved, which proved to provide protection of the treated specimens against dissolution in aqueous acidic solutions. Both ACC and am-SiO₂ protected the exposed surfaces through their strong interaction with the calcite rich building materials tested. The treatment with the NPs was successful because the surfaces probably participated in the mainly heterogeneous nucleation of ACC and am-SiO₂.

- Caner, E., Caner-Saltik, E.N. (2018) A practical method for preparing Ca(OH)₂ nanodispersions for the consolidation of archaeological calcareous stones, *Mediterranean Archaeology and Archaeometry*, Vol. 18, pp. 63-70.
- Chandra, S., Liping, W. (1999) Kolloidale Kieselsäure für das Festigen von Naturstein / Colloidal Silica in Stone Conservation. *RBM*, Vol.5, pp. 15-28.
- Faatz, M., Gröhn, F., Wegner, G. (2004) Amorphous Calcium Carbonate: Synthesis and Potential Intermediate in Biomineralization. *Adv. Mater.*, Vol. 16, pp. 996-1000.
- Fan, X., Batchelor-McAuley, C., Yang, M., Compton, R.G. (2022) Single calcite particle dissolution kinetics: revealing the influence of mass transport, *ACS Meas. Sci.* Vol. 2, pp. 422–429.
- Helmi, F.M., Abu Ayana Y.M., Tah, E.M. (2022) Sustainable biopolymers for protection of marble statue's head from Graeco roman period (case study) *Mediterranean Archaeology and Archaeometry*, Vol. 22, pp. 109-121.
- Ion, R.-M., Doncea, S.-M., Turcanu-Carutiu, D. (2018) Nanotechnologies in Cultural Heritage-Materials and Instruments for Diagnosis and Treatment. *Novel Nanomaterials*; Intechopen, London, UK.
- Ion, R.-M., Nyokong, T., Nwahara, N. (2018) Wood preservation with gold hydroxyapatite system. *Herit. Sci.* Vol. 6, pp. 37-46.
- Kanellopoulou, D.K., Vavouraki, A.I., Koutsoukos, P.G. (2019) Deterioration of Monument Building Materials: Mechanistic Models as Guides for Conservation Strategies, *Deterioration of Monument Building Materials: Mechanistic Models as Guides for Conservation Strategies: First International Conference, Revised Selected Papers, Part I*. Athens, Greece.
- Kazmierczak, T.F., Tomson, M.B., Nancollas, G.H. (1982) Crystal growth of calcium carbonate. A controlled composition kinetic study. *J Phys Chem.* Vol. 86, pp. 103-107.
- Lioliou, M.G., Paraskeva, C.A., Koutsoukos, P.G., Payatakes, A.C. (2007) Heterogeneous nucleation and growth of calcium carbonate on calcite and quartz, *Journal of Colloid and Interface Science* Vol. 308, pp. 421–428.
- Manoudis P.N., Gemenetzi, D., Karapanagiotis, I (2017) A comparative study of the wetting properties of a superhydrophobic siloxane material and rose petal *Scientific Culture*, Vol. 3, pp. 7-12.
- Phipps, J., Lorusso, M. (2001) Dissolution Behaviour of calcium carbonate in mildly acidic conditions. *The science of papermaking, Trans. of the XIIth Fund. Res. Symp. Oxford* (C.F. Baker, ed.), Manchester, UK.
- Rodriguez-Navarro C., Elert K., Ševčík R., (2016) Amorphous and crystalline calcium carbonate phases during carbonation of nanolimes: implications in heritage conservation, *CrystEngComm*, Vol.18, pp. 6594-6607.
- Sadat-Shojai, M., Ershad-Langroudi, A. (2009) Polymeric coatings for protection of historic monuments: Opportunities and challenges. *J. Applied Polymer Science*, Vol.112, pp. 2535-2551.
- Sierra-Fernandez, A., Gomez-Villalba, L.S., Rabanalb, M.E., Fort, R. (2017) New nanomaterials for applications in conservation and restoration of stony materials: A review, *Materiales de Construcción*, Vol. 67 (325) e107
- Singh, T.K., Jain, C.L., Sharma, S.K., Singh, S.S. (1999) Preparation of dispersed silica by hydrolysis of tetraethyl orthosilicate. *Indian J. Eng. Mater. Sci.*, Vol. 6, pp. 349-351.
- Spathis, P., Triantafyllidis, K., Prochaska, P., Karapanagiotis, I., Pavlidou, E., Stefanidou, M. (2018) Characterization and Properties of Silicate and Nanocomposite Coatings for the Protection of Dolomite Marble Against Weathering: Natural and Anthropogenic Hazards and Sustainable Preservation. *Proceedings of 10th International Symposium on the Conservation of Monuments in the Mediterranean Basin. Natural and Anthropogenic Hazards and Sustainable Preservation*, Athens, Greece.
- Storemyr, P., Wendler, E., Zehnder, K. (2001) Weathering and Conservation of Soapstone and Greenschist Used at Nidaros Cathedral (Norway), in: Lunde, Ø. & Gunnarsjaa, A. (eds.), *Report Raphael II Nidaros Cathedral Restoration Trondheim Norway 2000. EC Raphael Programme – European Heritage Laboratory. Report no. 2/2001, The Restoration Workshop of Nidaros Cathedral, Trondheim, Norway*, Oslo, Norway.
- Stuff, M., Rübner, K., Prinz, C., Rische, N., Chronz, M., Kühne, H.-C. (2020) Weathering and conservation of tuff stone, *EGU General Assembly 2020*, Online, 4–8 May 2020
- Syrmakezis, C.A. (2006) Seismic protection of historical structures and monuments. *Struct. Control Health Monit.*, Vol.13, pp. 958-979.
- Tesser, E., and Antonelli, F (2018) evaluation of silicone based products used in the past as today for the consolidation of venetian monumental stone surfaces. *Mediterranean Archaeology and Archaeometry*, Vol. 18, pp. 159-170.
- Wang, W., Wang, S., Liu, Q., Wang, X., Zhu, J., Luo, H., Ji, S. (2022) Study on the efficacy of amorphous calcium carbonate as a consolidant for calcareous matrix, *Herit. Sci.* Vol. 10, pp. 165-174.