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Scientific paper

ANANALYTICAL STUDY OF MARBLE CONSOLIDATION BY OXALATE PRECIPITATION USING DENSITY, FTIR AND POWDER-XRD MEASUREMENTS

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Abstract

Our recent study on consolidation of marble samples with the purpose of culture heritage protection occurred by periodical calcium oxalate precipitation on top of quasi parallelepipedic samples. The overall process consisting of three stages of treatment, starting with 5 % calcium acetate solution for 60 minutes at 20°C, a draining step at 70°C for 30 min, followed by a treatment with 5 % ammonium sulfate solution, it followed with the third stage which includes the treatment with 5% ammonium oxalate solution revealed a continuous density increace, determined using ethanol. As the natural samples had an initial density of 2.5871 g/cm^3, it increased up to 2.6980 g/cm^3 for 50 times treatments. The precipitation of oxalate on top of calcium carbonate substrate, in form of calcite, revealed two distinguished infra-red bands, at 1316 cm^{-1}and 1624 cm^{-1} unsymmetrically located around the carbonate one at 1426 cm^{-1}.The intensity of the bands was proportional to the number of treatments. The continuous surface coverage investigated in parallel by powder XRD evidenced the presence of whewellite crystallites deposited on top of calcite, and their intensity increasing as well with the number of treatments. This method exhibits a reliable oxalate coverage of marble sample surfaces which doesn't influence considerably their water solubility.

Key words: *calcium oxalate, marble, precipitation, density, FTIR, X- ray powder diffraction (XRD)*

1. INTRODUCTION

Marble is a material that is found constantly in the building, whether for structural purposes (columns, floors, etc.) or decorative (friezes, reliefs, statues, etc.). Marble is a noble material with a special charm and easily processed, but is sensitive to changes in natural atmospheric agents or others resulting from urban and industrial activity. Marble is formed through a process of metamorphic sedimentary rocks such as limestone and dolomite, and has a low porosity [1]. When exposed to the outside environment, these carbonate stone materials undergo wet weathering that irrevocably degrades the stone substrate. Thus to prevent the deterioration and degradation of stone as a result of erosion and weathering, is very important to choose adequate methods of conservation and protection which acknowledge the chemical and physical character of diverse stone lithotypes. An effective treatment may be considered as one that protects the carbonate materials from degradation mechanisms, while not causing any damage to the stone itself [2]. A suitable method has been identified in the use of the calcium oxalate method that imitates the natural patina observed on monuments where the underlying marble substrate is usually well conserved. In nature, this patina consists mainly of calcium oxalate which exists in two forms: monohydrate whewellite ($CaC_2O_4 \cdot H_2O$) and dehydrated weddellite ($CaC_2O_4 \cdot 2H_2O$). Formation of calcium oxalate on calcareous stone has been noted to penetrate deeply in an intergranular position or along micro fracture. [2-3]. Calcium oxalate compared to calcium carbonate is less soluble in the water [4].

Consolidation is considered to be one of major conservation interventions for building stones, sculptures, decorative surface, in attempt to prevent the deterioration and degradation of stone [5]. Besides the type of product used, the consolidation action achieved depends on the treatment methodology, which to a large extent can be described using parameters such as product concentration, solvent type, application process, and contact time.The product, solvent, and concentration are in general well managed in research protocols and reported in the published literature [6]. In our study we used three stages of treatment, starting with 5% calcium acetate solution followed by a treatment with 5% ammonium sulfate solution and 5% ammonium oxalate solution. In this way, crystallization centers are formed, which grow further as a consequence of the deposition of cations and anions present.

The chemical reaction is:

$$Ca(CH_3COO)_2 + (NH_4)_2 SO_4 \rightarrow CaSO_4 + 2NH_4 C_2H_3O_2 \quad (1)$$

$$CaSO_4 + (NH_4)_2C_2O_4 \rightarrow \downarrow CaC_2O_4 + (NH_4)_2SO_4 \quad (2)$$

The precipitation of oxalate on top of calcium carbonate substrate, in form of calcite, is assessed by the Fourier transform infrared spectroscopy (FTIR). Also, the continuous surface coverage investigated in parallel by powder XRD evidenced the presence of whewellite crystallites deposited on top of calcite, revealing their intensity increasing as well with the number of treatments. This method exhibits a reliable oxalate coverage of marble sample surfaces which doesn't influence considerably their water solubility.

2. EXPERIMENTAL

2.1. Reagents

All chemicals used were of analytical grade. The necessary reactants used for treatments of samples are: Calcium Acetate; Ammonium Sulphate and Ammonium Oxalate. The marble sample from the slabs of the Tirana Cultural Centre "The Pyramid" was used. The marble samples employed in this study are cut in parallelepiped form blocs with lengths of 25 ± 1mm, widths and thicknesses of 7 mm.

2.1.1. Sample preparation

To remove the attached dust, the prepared samples were dipped in distilled water for 2-3 hours followed by drying for 6 hours at 70 °C, 6 hours at

100°C and 12 hours at 125°C. While treating them by three chemical solutions (5%) [5], in order to form insoluble precipitates inside them. In our study were used three stages of treatment, starting with 5 % calcium acetate solution for 60 minutes at 20^0C, a draining step at 70°C, for 30 min, followed by a treatment with 5 % ammonium sulfate solution. After the application of the same draining procedure as previous, it followed with the third stage which includes the treatment with 5% ammonium oxalate solution $(NH_4)_2C_2O_4 \cdot H_2O$, followed by the same draining procedure. One sample was left untreated to be used as blank, other samples were subject of: 10, 20, 30, 40, 50 treatments respectively, revealing each time weight increase.

2.2. METHODS OF CHARACTERIZATION

2.2.1. Fourier Transforms Infrared Spectroscopy and X-Ray Powder Diffraction.

In previous spectroscopic studies, the response of FT- Raman spectroscopy to the detection of non-transition metal (Groups I and II) oxalates, including calcium oxalate mono-hydrate and dihydrate and magnesium oxalate dihydrate, was assessed [7]. In this paper we used Bruker Tensor 27 FTIR to assess the precipitation of oxalate on top of calcium carbonate substrate, in form of calcite. In the present study, typically 14220 interferograms were collected covering a spectral range from 4000 to 800 cm^{-1} at a resolution of 4 cm^{-1} with standard KBr beam splitter. Interferometer: Rock Solid, Permanent aligned, high stability, Scan Speed 3 velocities, 2.2 - 20 kHz [8-11]. Also an analysis was made with X-Ray Powder Diffraction evidenced the presence of whewellite crystallites deposited on top of calcite. To determine the marble samples density is used the Archimedes balance which revealed a continuous density increase, determined using ethanol.

3. RESULTS AND DISCUSSION

In this paper we investigated the precipitation of oxalate on top of calcium carbonate substrate, in form of calcite in the marble samples. We used three stages of treatment, one sample was left untreated to be used as blank, other samples were subject of: 10, 20, 30, 40, 50 treatments respectively, revealing each time weight increas. The natural samples had aninitial density of 2.5871 g/cm^3, it increased up to 2.6980 g/cm^3 for 50 times treatments. Density is a direct reflection of the material porosity. During the treatments was formed oxalate on top of calcium carbonate substrate, which is more insoluble, and morphology, shinning, etc. In order to prove the assumptions from light microscopic images above, the marble samples subject of carbonate substrate, which is more insoluble, and closes the pores and material structural defects.

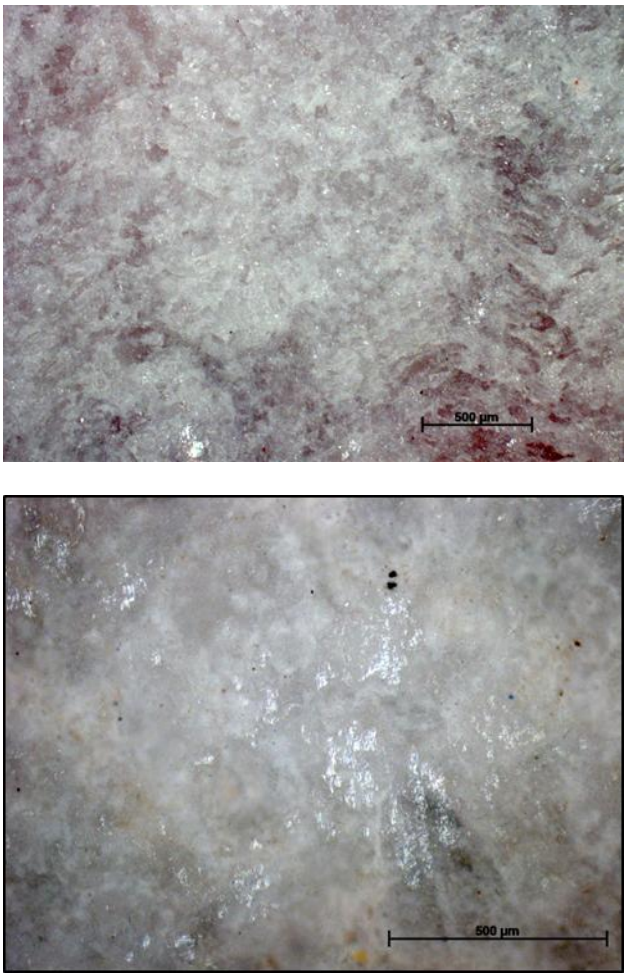

Figure 1: Light microscope images of: (a) untreated, (b) 50X treated marble sample, taken with a 50X magnification

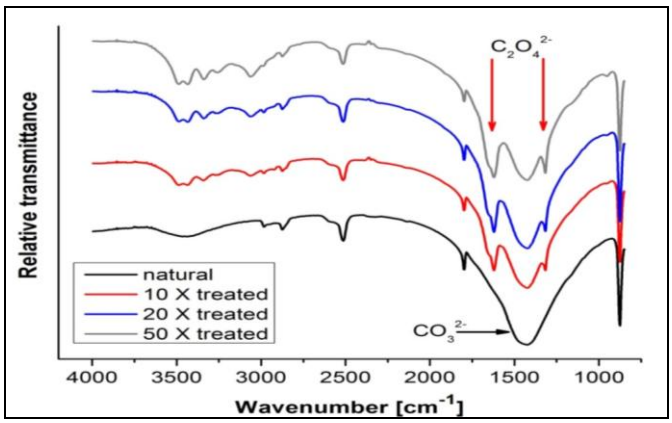

Figure 2: FT-IR spectra of natural and treated marble samples

The comparison of the light microscope images of (a) untreated and (b) 50X treated marble sample, as shown by fig. 1, reveals a clear difference between them. The presence of compact oxalate crystalline layer on top of marble surface, typical for the treated sample is obvious from its visual properties, such as treatments respectively, were analyzed further by Fourier Transform Infrared Spectroscopy. FT-IR spectra of marble samples are presented in Figure 2. The presence of oxalateprecipitated on top of calcium carbonate substrate, revealed two distinguished infra-red bands, at 1316 cm^{-1} and 1624 cm^{-1} unsymmetrically located around the carbonate one at 1426 cm^{-1}. Further detailed investigations by powder XRD are shown in Figure 3 by comparing the measured powder patterns of natural marble (untreated) and treated samples (10X, 20X and 50X). The natural sample consists mainly of Calcite, since the calculated powder pattern (lowest diffratogramme) fits well with powder pattern of the natural marble sample. A better overview of it is exhibited in figure 4. As a consequence of the sample treatments as described above, oxalate monohydrate (whewellite) crystals are formed as shown by the additional reflections compared to the natural sample.

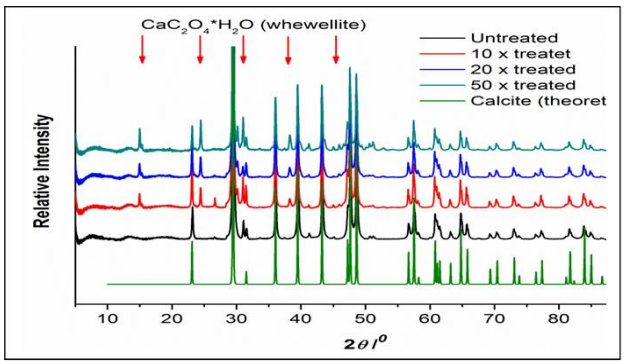

Figure 3: XRD patterns of the natural and treated marble samples compared to the calculated Calcite pattern

The intensity of the reflections is proportional to the quantity of oxalate formed, therefore proportional to the number of treatments. This method exhibits a reliable oxalate coverage of marble sample surfaces which doesn't influence considerably their water solubility.

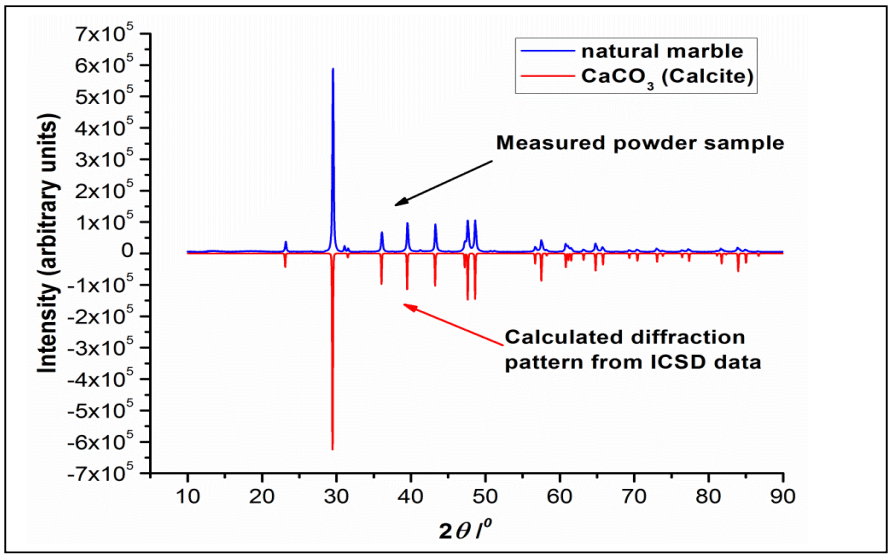

Figure 4: Comparison of the measured powder sample of natural marble and calculated diffraction pattern of Calcite from ICSD data.

4. CONCLUSIONS

Prevention of the deterioration and degradation of stone as a result of erosion and weatheringhas been the objective of this study. The marble sample from the slabs of the Tirana Cultural Centre "The Pyramid" was used. The marble samples consolidation is done in three stages treatment with chemical solutions (5%) in order to form insoluble precipitates inside them. All samples were subject of: 10, 20, 30, 40, and 50 treatments. In this way, crystallization centers are formed, which grow further as a consequence of the deposition of cations and anions present. After each treatment we used the Archimedes balance which revealed a continuous density increase, determined using ethanol.The natural samples had an initial density of 2.5871 g/cm^3, it increased up to 2.6980 g/cm^3 for 50 times treatments. Calcium oxalate formed inside pores is highly insoluble; its solubility in water at a temperature of 13°C is 0.00067 g/100 g water [12]. Methods of characterization are FTIR, X-ray powder diffraction (XRD). Through of FTIR we investigated the precipitation of oxalate on top of calcium carbonate substrate, in form of calcite and with X-ray powder diffraction (XRD) evidenced the presence of whewellite crystallites deposited on top of calcite, where their intensity increased as well with the number of treatments. With this method we confirmed that by increasing of the number of chemical treatments an overall reduction of the marble sample porosity can be achieved as a result of the formation of the precipitate formation of calcium oxalate.

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