Methods of Consolidation and Protection of Pentelic Marble

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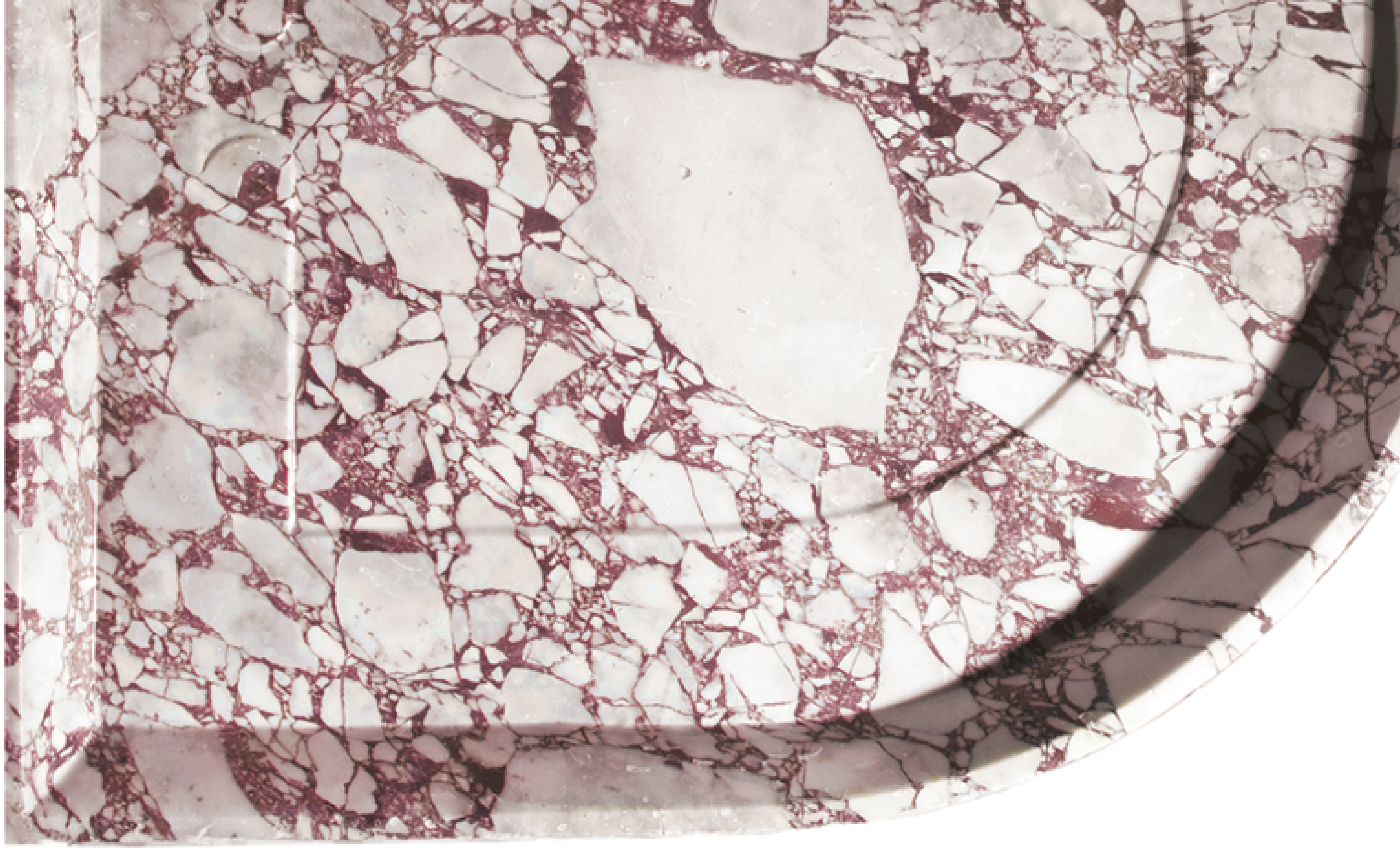

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Katja Marasović

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METHODS OF CONSOLIDATION AND PROTECTION OF PENTELIC MARBLE

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Abstract

The purpose of this research study was to investigate the performance of the consolidation and the protective effect of treatments carried out on Pentelic marble specimens exhibiting granular disaggregation. Consolidation materials and techniques were applied and evaluated on weathered samples of Pentelic marble.
"Reinforced lime" and a nano-dispersion of calcium hydroxide were selected as consolidants (with and without sodium stearate) and compared. Before consolidation, the specimens were examined in order to assess their state of conservation, using optical microscopy, infrared spectroscopy (FT-IR) and electron scanning microscopy coupled with microanalysis (SEM-EDX). The consolidation treatments were assessed using SEM-EDX, a portable spectrophotometer, contact angle measurements and sonication treatment in order to study the degree of adhesion with the substrate.
The results showed that the nano-dispersion of calcium hydroxide with the addition of sodium stearate exhibited the best surface consolidation results. It can therefore be applied for both consolidation and protection treatments of Pentelic marble.

Keywords
pentelic marble, calcium hydroxide nano-dispersion, consolidation

1. Introduction

Pentelic marble is a building material of great interest in the field of Monument Protection, as it is used in several monuments throughout the region of Greece. Furthermore, it has been used in monuments and historical building throughout history, ranging from antiquity, dating back to the classical era, up to relevantly recent structures, such as neoclassical buildings. Examples of buildings structured or adorned with Pentelic marble are of great cultural significance, such as the Acropolis monuments (MARAVELAKI-KALAITZAKI 2005, 187-198), the Hephaistos Temple in the Ancient Athenian Agora (CRAIG, CRAIG 1972, 401-403), the Poseidon Temple in Sounion and more recently the Academy of Athens, the National Technical University of Athens, and other important neoclassical buildings (KORRES 2001).

Pentelic marble was mined from the quarries of the Penteli mountain range. In antiquity the most important quarry was that of "Σπηλιά" located in the southwest part of the Penteli mountain area (MERTZANIS *et al.* 2004, 216). This quarry was in constant use until the 70s when its use was prohibited by law for the minimization of environmental impacts and protection of the area (Greek Legislation Law 386/76) (PAVLOU 1995). Today, the mining of high quality white marble is performed from the quarry of "Διονυσοβούνι" a quarry located at the north extension of the Pentelic mountain range, with the same metamorphic structure (KORRES 2001, 71, 78, 94).

Pentelic marble is well known for its high durability and longevity. Nowadays the Pentelic marble of monuments exposed to heavily polluted environments, such as the atmosphere of Athens' centre, has become more susceptible to decay, jeopardizing its longevity. The main factors causing the decay of Pentelic marbles are acidic attack, wetting-drying cycles, temperature variation cycles, wind erosion, the presence of salts, incompatible restoration materials and biological attack.

One of the main kinds of decay exhibited by Pentelic marble elements in buildings is granular disaggregation (also called surface sugaring), causing aesthetic problems, but more importantly the loss of cohesion of marble grains on the surface exposed to the environmental factors, leading to crumbling and in some cases detachment of marble elements. Granular disaggregation is due to environmental factors, such as temperature variations and acid rain as well as endogenous factors, such as the anisotropy of the material itself. Granular disaggregation is triggered by environmental thermal excursions, such as day/night variations (especially for marble elements directly exposed to solar radiation). Temperature variations cause deformation of calcite crystals, due to their unusual anisotropic behavior; they expand parallel to the crystallographic c-axis and contract perpendicularly to the same axis. As a result, micro-cracks open at the boundaries between grains that consequently lose cohesion and become prone to detachment. This latter aspect further threatens marble durability, because, through the newly developed micro-cracks, clean and acid rainwater, salt-rich rising damp, as well as atmospheric gaseous pollutants, can penetrate into the marble, thus exacerbating the related weathering phenomena (e.g., calcite dissolution, gypsum formation and salt crystallization) (SASSONI, FRANZONI 2014, 1893-1906; SASSONI, GRAZIANI, FRANZONI 2015, 1145-1157).

Several materials have been used in the past for the consolidation of marble surfaces. A suspension or a solution of barium hydroxide, sometimes with the addition of calcium hydroxide or urea has been used in the past for the consolidation of stones and marbles. Barium hydroxide, reacting with the carbon dioxide in the atmosphere, is transformed into barium carbonate and water. Some studies concerning barium hydroxide initially showed good results; however the sedimentation of the newly formed crystals was confined to the outer surface layers, leading to flaking in contact with the atmosphere; low connection capability between the stone particles (grains, crystals) ranks highly among its drawbacks. Casein and its products have also been used in the past for the consolidation of marble, however its presence induces surface bio-colonization and therefore extensive biological attack of the marble surface (SKOULIKIDIS 2000, 23-25; SKOULIKIDIS, VASSILIOU, TSAKONA 2005, 28-33).

Organic polymeric consolidants have been used in recent years, however they are considered completely unsuitable for marble consolidation; stability and durability are the main issues, which make organic polymeric treatments generally unsuitable for marble consolidation, in addition to their lack of chromatic compatibility (SASSONI, FRANZONI 2014, 1893-1906).

Silicate consolidants, such as ethyl silicate, are reported to provide a good immobilization of calcite grains, thanks to the deposition of silica gel in intergranular fissures. However, no chemical bonding between silica gel and marble occurs, with scarce mechanical improvement and effectiveness over time (SASSONI, GRAZIANI, FRANZONI 2015, 1145-1157).

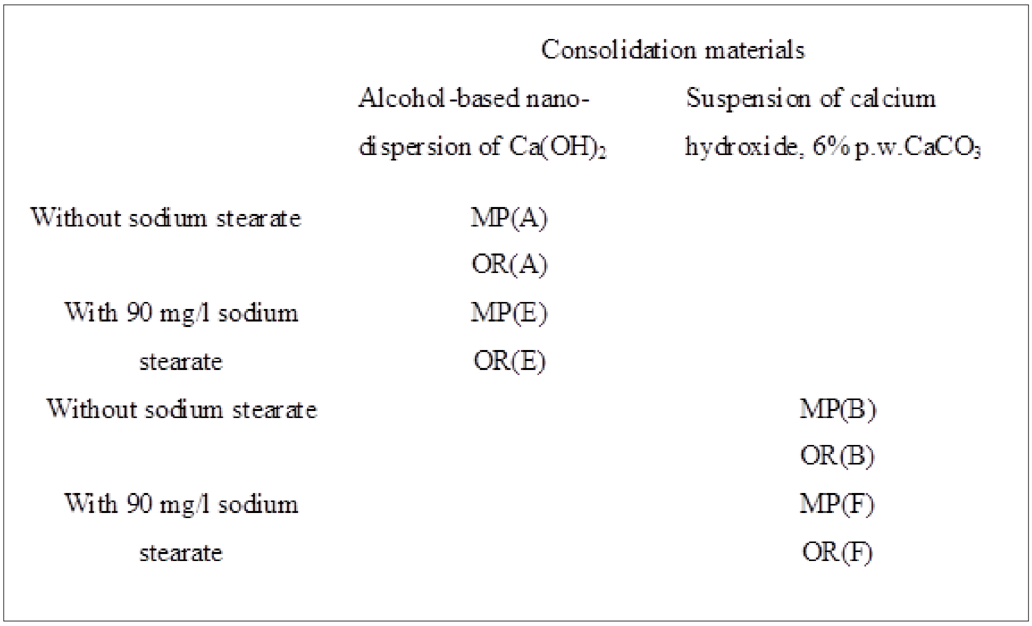
More recently, researchers have examined the use of ammonium oxalate (AmOx) treatments. AmOx treatments were first employed in order to make the surface it was applied to acid-resistant through a passivating treatment, by the formation of calcium oxalate, through the reaction of AmOx with the calcite of the marble. This is considered particularly advantageous and important in the case of porous calcareous materials exposed outdoors, particularly in polluted urban centers. Although encouraging results have been reported regarding the efficacy of AmOx, calcium oxalate formation has been found to be patchy on the marble surface and further research is required (MATTEINI 2008, 13-27; CHAROLA, CENTENO, NORMANDIN 2010, 29-44).

Sassoni *et al.* proposed the use of ammonium phosphate in order to form hydroxyapatite (HAP) inside marble micro-cracks. The results of the study indicate remarkable consolidation of weathered marble, with only slight alterations in pore size distribution and color change, thus providing much better results than either ethyl silicate or ammonium oxalate. However, studies regarding HAP nucleation and growth over calcite have pointed out that the effectiveness of the HAP coating to prevent dissolution of marble is partially limited by the HAP layer porosity and incomplete coverage of the marble surface (SASSONI, GRAZIANI, FRANZONI 2015, 1145-1157).

Lime-based consolidants are compatible and have been extensively used until the present. When calcium hydrate comes in contact with the atmosphere's carbon dioxide, it is transformed into calcite (a part of which is aragonite); this is the reason for lime-based consolidants being ranked very high amongst the consolidation materials used for calcite stones and marble surfaces. The product of the reaction is chemically and crystallographically similar to the calcium carbonate of marble; however it presents microstructure characteristics and mechanical properties different to the calcium carbonate of marble. The use of lime however presents disadvantages; it presents a very low carbonation rate, carbonation is not extended in the depth of the material and even when carbonation is complete, the mechanical strength and hardness values are quite low. According to Skoulikidis *et al.* the disadvantages of lime are overcome with the use of "reinforced lime", namely the addition of limestone powder, which accelerates the reaction; the addition of 6% $CaCO_3$ to plain lime increases the poor mechanical resistance of the $CaCO_3$, (produced by the reaction of atmospheric CO_2 and the lime), because of the acceleration of the reaction and the subsequent small crystals of $CaCO_3$ and facilitates the precipitation of $CaCO_3$ to the bulk of the mass of lime (SKOULIKIDIS, VASSILIOU, TSAKONA 2005, 28-33).

Caner observed that the addition of sodium stearate in low concentrations to a nano-dispersive calcium hydroxide solution increased the size and shape of calcite particles formed and facilitated efficient bonding in the cracks of the limestone consolidated, without affecting the stability of the solution (CANER 2011, 89, 109).

In this research study the performance of the consolidating and protective effect of treatments carried out on Pentelic marble specimens was investigated.



	Consolidation materials	
	Alcohol-based nano-dispersion of $Ca(OH)_2$	Suspension of calcium hydroxide, 6% p.w. $CaCO_3$
Without sodium stearate	MP(A) OR(A)	
With 90 mg/l sodium stearate	MP(E) OR(E)	
Without sodium stearate		MP(B) OR(B)
With 90 mg/l sodium stearate		MP(F) OR(F)

Fig. 1. Consolidation treatments

Consolidation materials and techniques were applied and evaluated on samples of Pentelic marble, deriving from two different restoration periods of the early and mid-20th century. The consolidation materials selected were one traditional type, currently used in the restoration of Pentelic marble, and one novel nano-material in order to compare their effectiveness.

2. Materials and methods

2.1. Sample description

The samples used in this experimental study were Pentelic marble specimens from two different restoration periods and present granular disaggregation. The first restoration work was in the early 20th century. These samples are coded MP and the sample dimensions were 1.35 cm x 3 cm x 1 cm ±1 mm. The second restoration period was in the mid-20th century. These samples are coded OR and the sample dimensions were 2 cm x 4 cm x 0.8 cm ±1 mm. All samples used were exposed outdoor until present to the polluted atmosphere of Athens and to environmental factors, the same factors affecting many monuments of the Athens center.

2.2. Consolidation materials and techniques

Two consolidation materials were selected in order to compare their effectiveness; a solution of hydrated lime with the addition of 6% p.w. $CaCO_3$ (reinforced lime), used until today, and an application of a novel nano-dispersion of calcium hydroxide, in a concentration of 15 g/l. Furthermore, the effect of the addition of sodium stearate (sodium stearate: $C_{17}H_{35}CO_2Na$) was examined by the addition of 90 mg/l to both materials for some applications (Fig. 1), in order to validate whether its use will assist in better formed calcite particles and facilitate efficient bonding. In order to ensure a homogenous and reproducible dispersion, the calcium hydroxide nano-dispersion was sonicated in a sonication device (VCX 750 της εταιρείας SONICS & MATERIALS, INC). The addition of sodium hydroxide was also followed by sonication with the same device.

The reaction leading to consolidation is the same for both materials:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (Eq.1)$$

The application of the consolidation treatments was conducted via spray applications, in order to simulate real treatment conditions. The spray application was done at a 15 cm distance from the marble surface. The nano-dispersion consolidation treatments (A&E) were applied 2 per week for 14 days (4 treatments in total), whereas the reinforced lime treatments (B&F) were implemented 2 per day for 20 days (40 treatments in total, as done in current practice). The total number of applications was calculated for each material in order for the total quantity of deposited lime to be comparable.

The treated samples were put in a vessel with 75% relative humidity for two months (supersaturated solution of NH_4Cl) in order to ensure the complete carbonation of the treated samples and the conversion of the calcium hydroxide to calcite (GOMEZ-VILLALBA, LOPEZ-ARCE, ALVAREZ DE BUERGO 2011, 1249-1254; CANER 2011, 109).

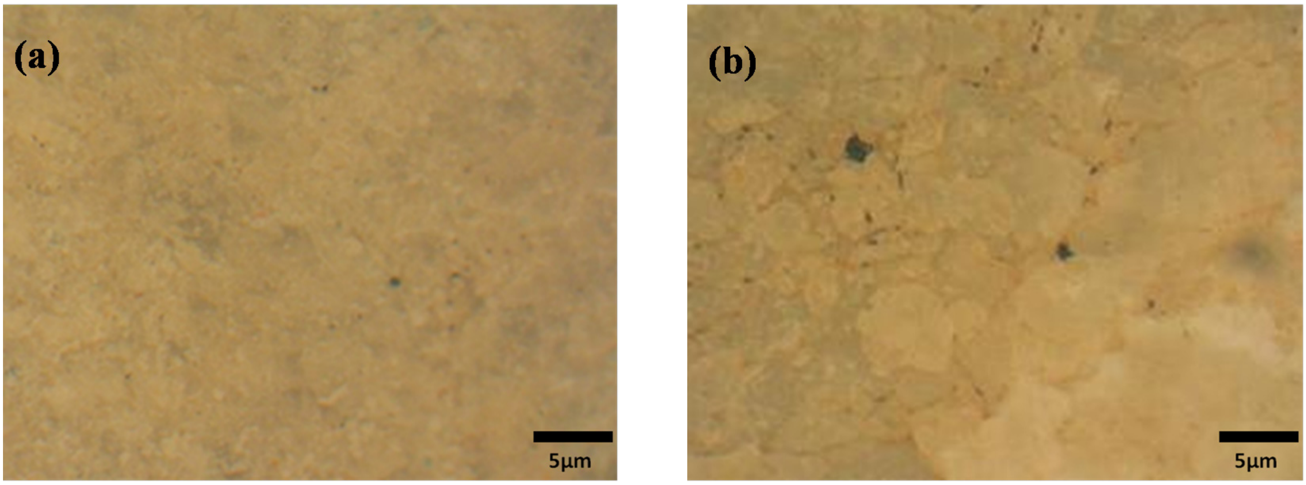


Fig. 2. Optical microscopy images of both marble sample types before consolidation treatments, a) MP x120, b) ORx120

2.3. Evaluation techniques

All samples were examined before the application of the selected consolidation treatments, in order to examine their state of conservation and the main exhibited decay, as well as after the consolidation treatments, in order to assess their efficacy.

Before the application of the consolidation treatments, the specimens were immersed in deionized water in order to remove dirt, loose deposits and gypsum (WT). The surface of the marble samples (WT) was then examined microscopically via optical digital microscopy (Scopeman Moritex microscope) and via stereomicroscopy (Leica MZ6). Scanning Electron Microscopy (SEM-EDX) was employed in order to examine the untreated marble surface and detect the type of decay of the specimens. The scanning electron microscope used was a Quanta 200 Fei and the acceleration voltage during the procedure was 25-30 KV. The software EDX Genesis was used for the X-ray microanalysis. Infrared spectroscopy (FT-IR) was conducted in order to detect decay products on the marble surface, through the analysis of a small amount taken from the marble surface (FT-IR Biorad Excalibur FTS 3000MX).

Microscopic examination of the marble surfaces was performed after the consolidation treatments in order to assess the effectiveness of the treatments and the state of the consolidated surface, as described above. SEM-EDAX was conducted in order to examine the consolidated surface and the consolidation products, as well as to determine whether the consolidation treatments resulted in any unwanted and possibly harmful by-products. All samples were weighed before ($W_{initial}$) and after the consolidation treatments (W_{final}), in order to estimate the mass gain due to consolidation and calcite crystal formation.

Furthermore, a portable spectrophotometer was used before and after the treatments in order to evaluate the variation of the chromatic parameters adopting the CIELab system (Dr Lange Color Pen LMG 159/160).

The applied consolidation treatments were also assessed through contact angle measurements, in order to examine whether the applied treatments resulted in a change of the contact angle. Contact angle measurements were conducted with untreated (WT) and consolidated specimens in compliance with EN 15802:2010.

The adhesion degree of the consolidation materials with the marble substrate was studied through sonication treatments. The consolidation effect of the proposed treatments was assessed via sonication tests (RODRIQUEZ-NAVARRO *et al.* 2003, 2182-2193; DASKALAKIS *et al.* 2013, 409-423; DASKALAKIS *et al.* 2015, 73-84). Consolidated samples as well as untreated samples were immersed in deionized water in an upright position. Sonication occurred for 5min (20 KHz, Emmi 30 HC EMAG) and the samples were immediately rinsed with deionized water and dried at 60 °C for 24 h prior to weighing. The process was repeated five times. Results are presented as weight loss per cycle ($W_{i-1} – W_i$, i:cycle number). The weight of each sample was measured before each sonication cycle (W_{i-1}) and after each sonication cycle (W_i).

3. Results and discussion

3.1. State of preservation

The untreated marble samples (WT) were first examined in order to evaluate their state of preservation. The main type of decay detected through optical microscopy was the extended granular disaggregation on the surface of the marble specimens (Fig. 2a, Fig. 2b). All MP specimens, although exposed to the environment at

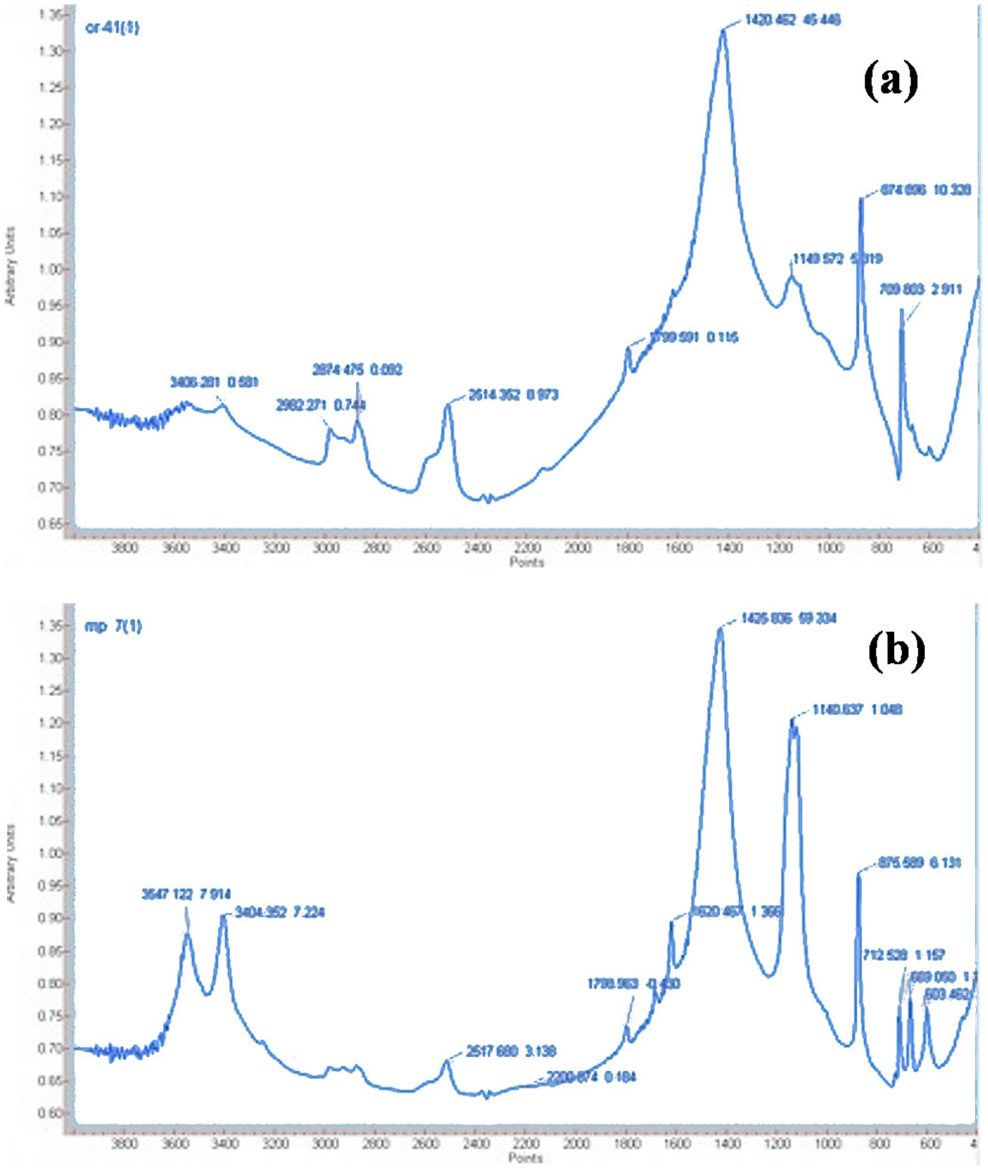


Fig. 3.
FT-IR results,
a) FT-IR results for marble samples MP,
b) FT-IR results for marble samples OR

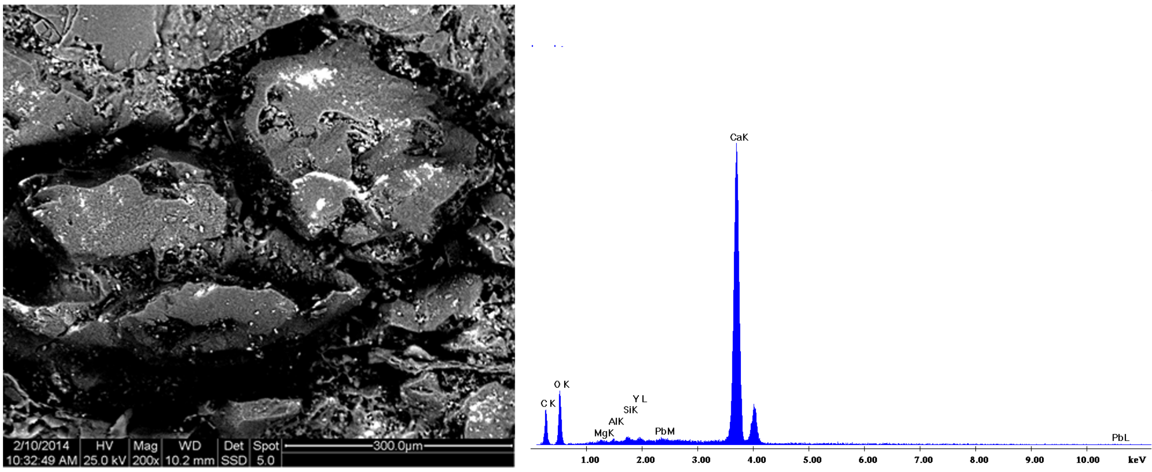
least three decades more than the OR specimens, show a better state of preservation. This can be attributed to the different exposure conditions. Bio-deterioration was noticed in all samples.

FT-IR was employed in order to identify decay products on the marble samples (Fig. 3a, Fig. 3b). Gypsum was detected in all samples, both MP and OR, due to the sulphation process, generated from the polluted urban environment the samples have been exposed to for decades. Organic compounds are also detected probably due to the hydrocarbons of the urban atmosphere.

Scanning Electron Microscopy (SEM) confirms the optical microscopy results regarding the main type of decay, as granular disaggregation is observed throughout the surface (Fig. 4). Microanalysis via EDAX showed traces of sulphur and lead, as well as a small percentage of alumino-silicate contaminants (Fig. 4). The alumino-silicate contaminants are generated from the material itself or deposited from the atmosphere, and the traces of lead are probably due to the sealing with lead in the procedure since ancient times.

3.2. Assessment of consolidation treatments

The marble specimens were evaluated after the consolidation treatments. From the microscopic examination (SEM) the inhomogeneous distribution of the neo-formed calcite crystals on the surface of the samples treated with the reinforced lime (Treatments B&F) was noticed; the formed crystals present a different size and shape from the original marble crystals (Fig. 5a). The samples treated with the nano-dispersion of calcium hydroxide (A&E) presented an improved deposition covering the entire marble surface; the formation of calcite crystals is homogeneous and the formed calcite crystals present a better adhesion to the marble surface, covering the intercrystalline voids



C	**13.34**
O	**45.12**
Mg	**0.79**
Al	**0.46**
Si	**1.37**
Y	**0.91**
S	**0.22**
Pb	**0.64**
Ca	**36.71**
Fe	**0.45**

Fig. 4. SEM-EDX results of untreated samples (WT)

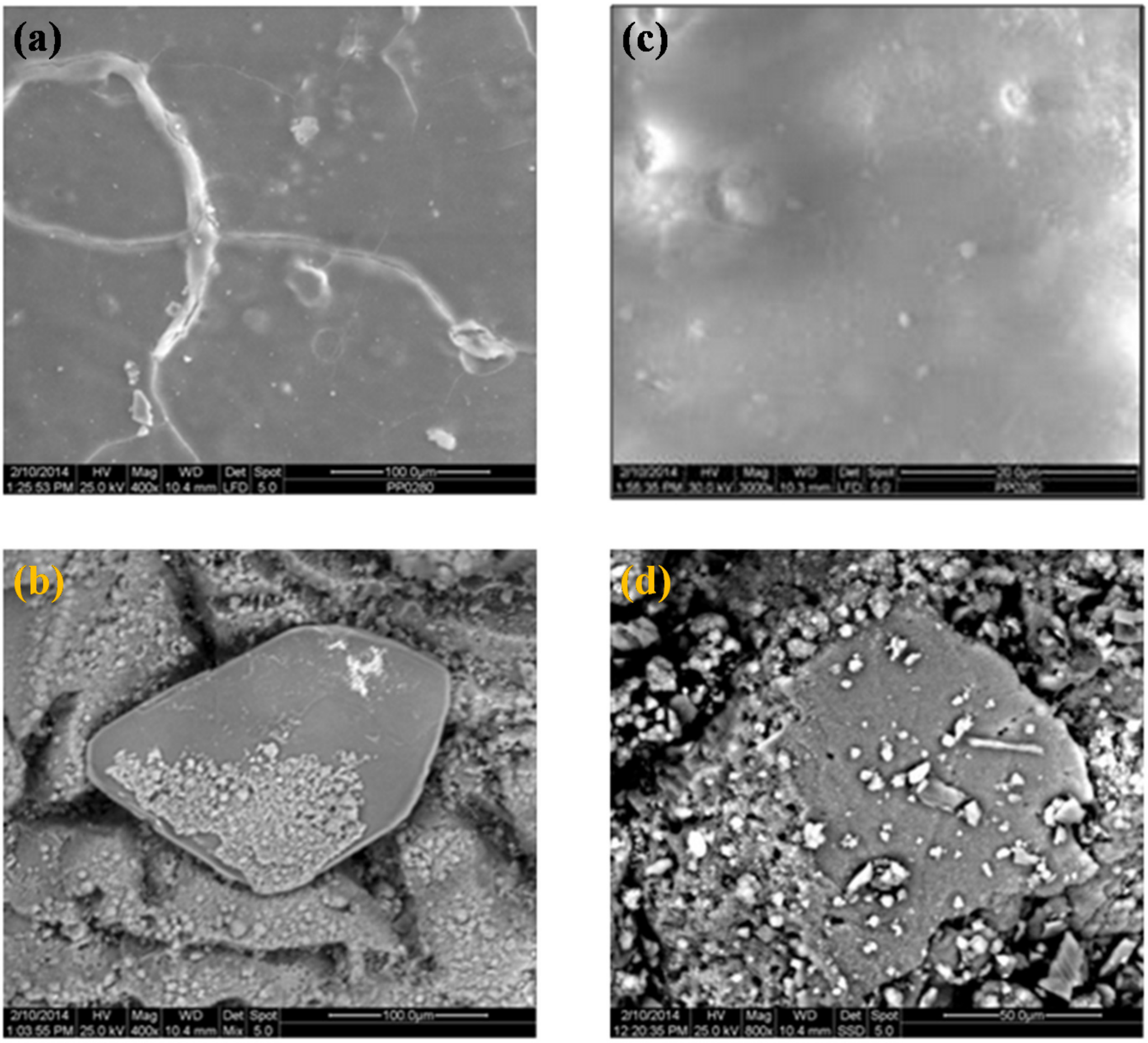
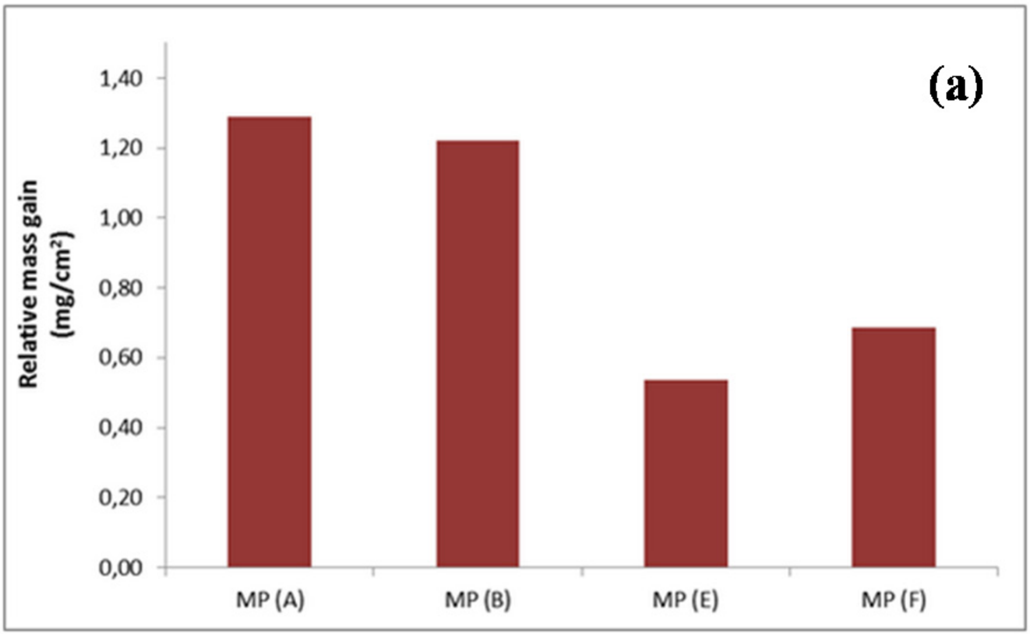


Fig. 5. SEM images of consolidated marble samples, a) SEM image of OR sample consolidated with (A) treatment x400, b) SEM image of OR sample consolidated with (B) treatment x400, c) SEM image of OR sample consolidated with (E) treatment x3000, d) SEM image of OR samples consolidated with (F) treatment x800



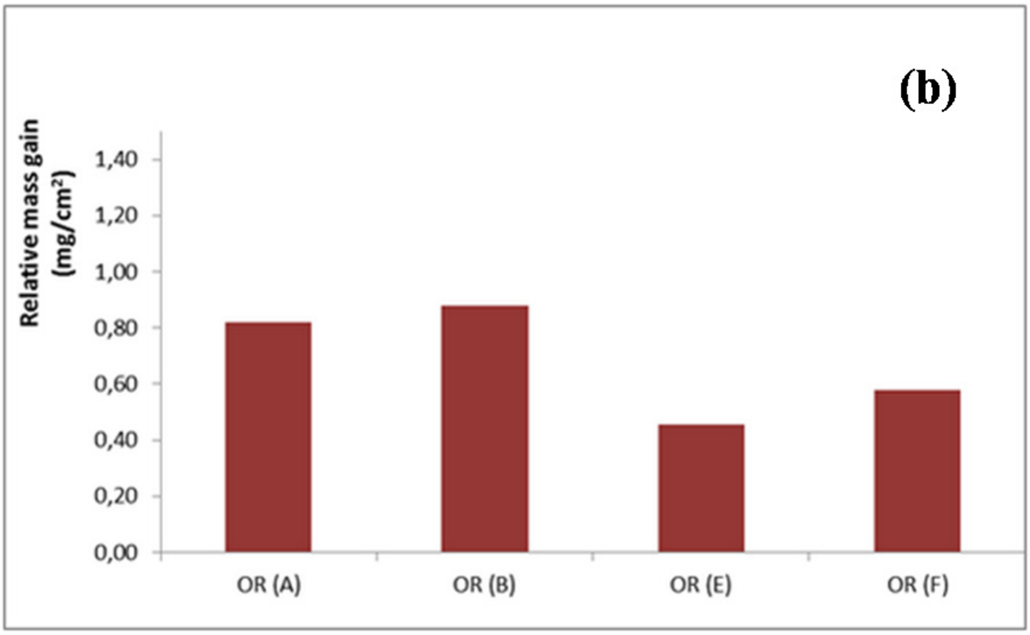


Fig. 6.
Relative mass gain due to consolidation treatments: a) Relative mass gain (mg/cm2) due to consolidation treatments on MP samples, b) Relative mass gain (mg/cm2) due to consolidation treatments on OR

(Fig. 5b). Furthermore, the use of sodium stearate along with nano-dispersion of calcium hydroxide reduces considerably microcracking and results in an even more homogenous consolidated surface (Fig. 5c).

All marble specimen masses were measured before the consolidation treatments and after the consolidation treatments, in order to determine the relative mass gain exhibited due to the applied consolidation treatment (after complete carbonation). The results are presented in Fig.6 as relative mass gain and have been derived from the weight gain exhibited by each sample in relation to the total consolidated surface (g/cm^2). The samples treated with reinforced lime (Treatments B&F) exhibit a quite similar mass gain, with small deviations, to the samples treated with the nano-dispersion of calcium hydroxide (A&E). When the treatments were applied without the addition of sodium stearate (A&B) they presented a greater mass gain than the treatments applied with the addition of sodium stearate (E&F).

Sonication treatments were employed in order to examine the degree of adhesion of the consolidation materials. Sonication tests proved that all treatments increase the cohesion of the marble surface, in comparison to the untreated specimens, thus resulting in a more solid marble surface, withstanding sonication forces. Results here are presented as the cumulative weight loss in relation to sonication cycles for consolidated marble samples. In particular, as seen in Fig. 7a and Fig. 7b, the improvement

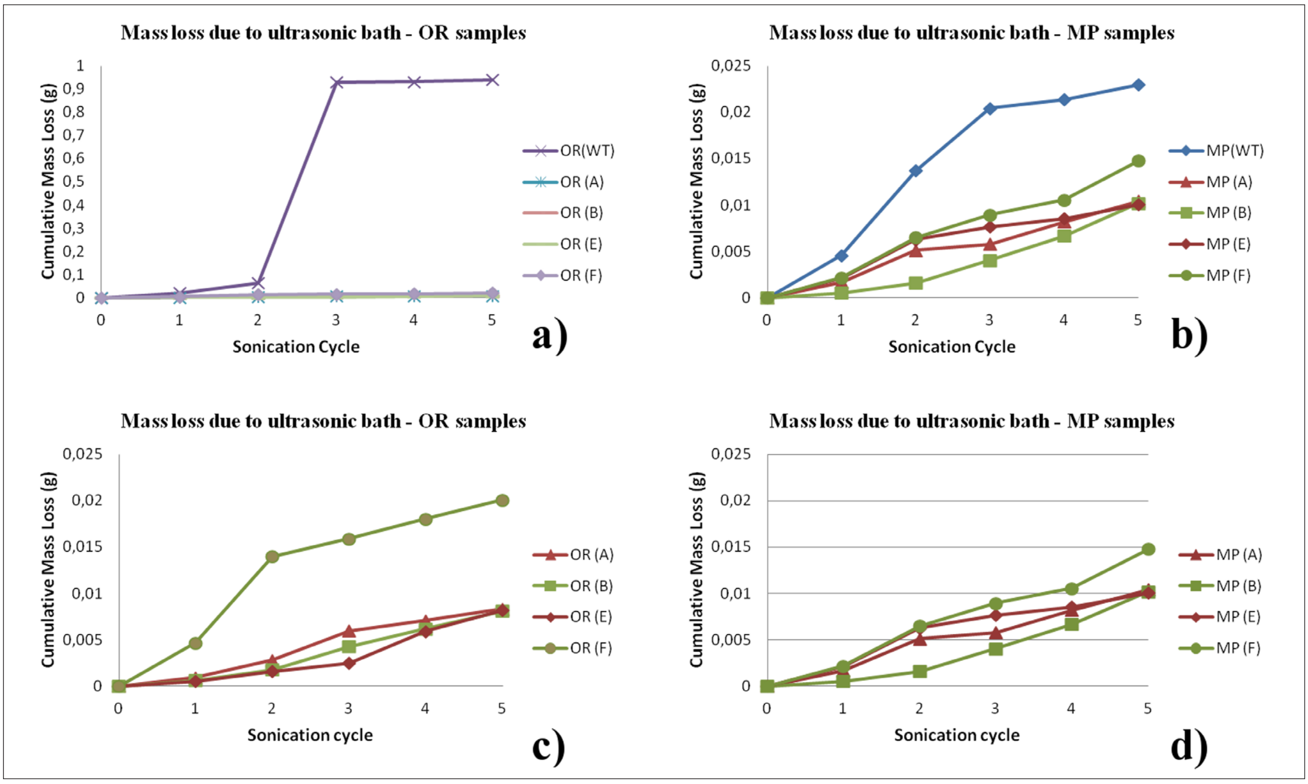


Fig. 7. Cumulative mass loss (g) due to ultrasonic bath treatments by cycle, a) OR samples treated and untreated, b) MP samples treated and untreated, c) OR samples only treated, d) treated MP and OR samples comparison

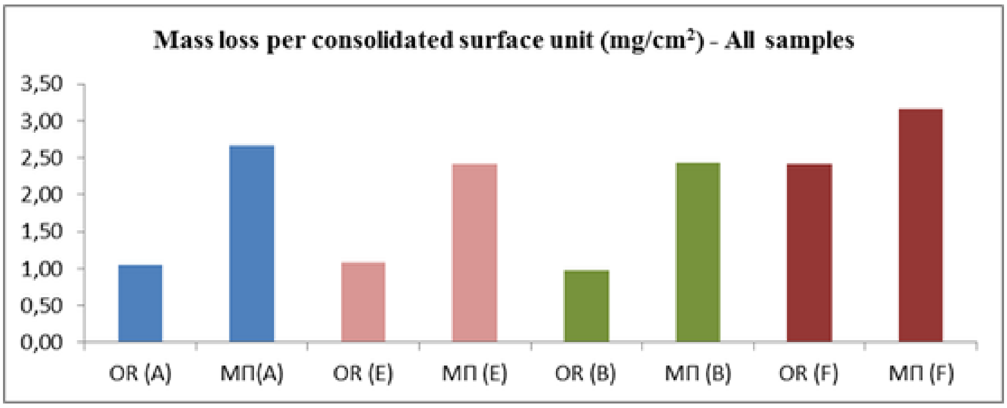


Fig. 8.
Total mass loss per consolidated surface at the end of the sonication cycles (mg/cm2)

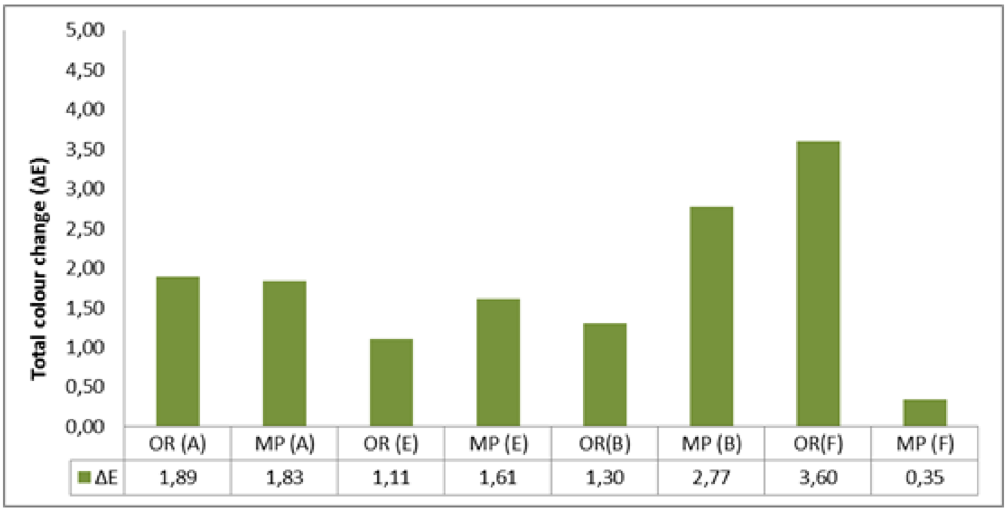


Fig. 9.
Total color variation for all treated samples (ΔE)

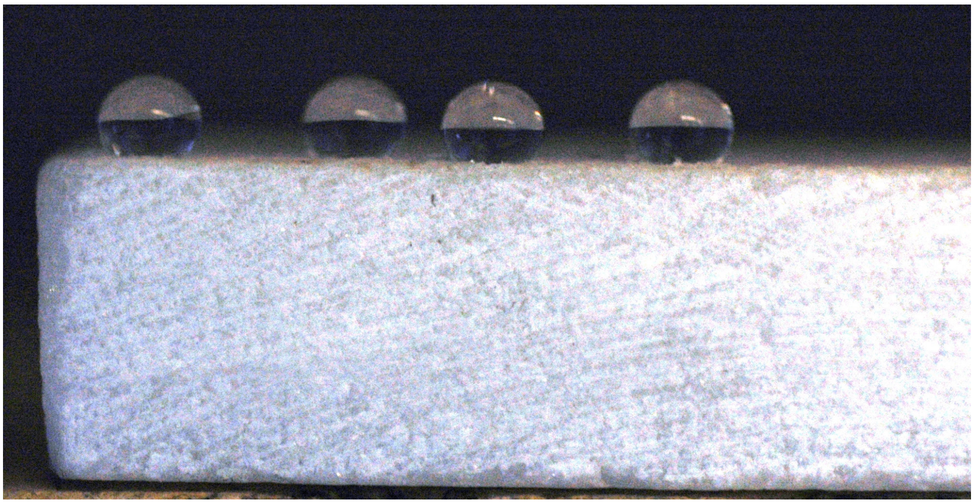


Fig. 10.
Static contact angle measurements

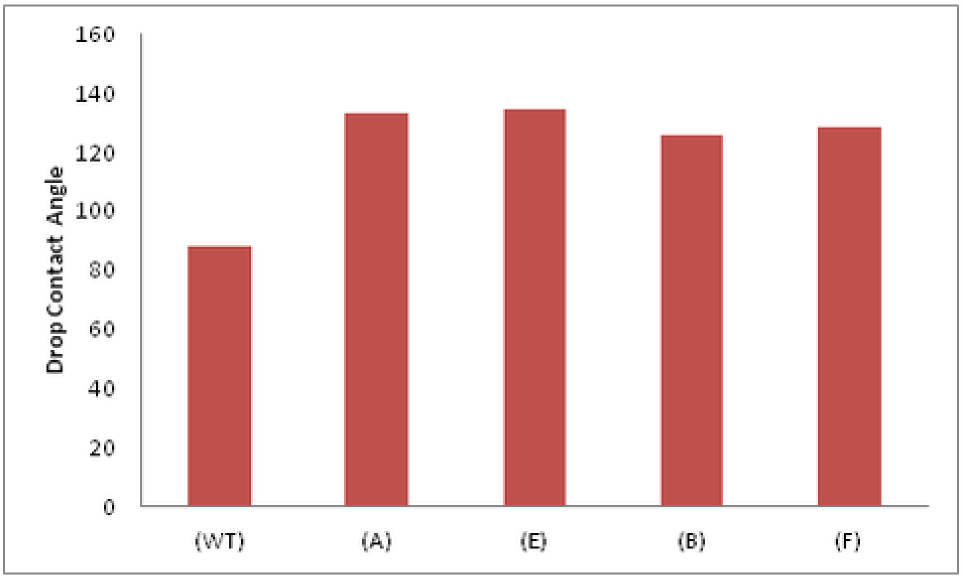


Fig. 11.
Drop contact angle measurements for untreated marble sample (WT) and consolidated samples

to the cohesion of the samples' surface is considerable, especially for samples OR, which were in a worse state of preservation than the MP samples. In general, as shown in Fig. 7b and Fig. 7c it seems that the addition of sodium stearate does not have a beneficial effect on the mass loss measured, especially in the case of reinforced lime (B&F), where samples treated with reinforced lime exhibit a lower mass loss than samples treated with the solution of reinforced lime and the addition of sodium stearate. Both consolidation treatments have a larger impact on the OR samples, which were in a worse state of preservation before the applied treatments (Fig. 7d). Furthermore, as seen in Fig. 8, the OR samples present a lower total mass loss per surface than the MP samples, indicating that the consolidation treatments are more effective on surfaces presenting a higher degree of granular disaggregation.

Colorimetric measurements were taken before and after each consolidation treatment in order to examine the chromatic variations that each consolidation material induced. All samples presented total colour difference values lower than 5 (Fig. 9) and are considered acceptable. A consolidation treatment can be considered acceptable if the total colour change (ΔE) is less than 5 (DELGADO RODRIGUES 2007, 32-43). The same treatments seem to induce a different colour change with different degree of decay; for example, treatment (F) induces an extremely low colour change on MP samples and a relatively high colour change on samples OR. The use of the nano-lime dispersion (E) presents the lowest colour change for both sample types.

Static contact angle measurements were carried out before and after the consolidation treatments (Fig. 10). In all samples the contact angle increased after treatment, resulting in values over 90° in all cases. The samples consolidated with the novel nano-dispersion of calcium hydroxide (A) exhibited contact angle almost 10^{o} higher than the samples consolidated with the reinforced lime (B). The use of reinforced lime with the addition of sodium stearate (F) results in slightly higher contact angle, however still lower than the contact angle exhibited by the samples consolidated with the novel nano-dispersion of calcium hydroxide (A). The highest values of static contact angle were exhibited by the samples treated with the nano-dispersion of calcium hydroxide with the addition of sodium stearate (E), thus having protective effect on the marble surface (Fig. 11).

4. Conclusions

The consolidation treatment with the nano-dispersion of calcium hydroxide presented a better total performance than the current traditional consolidation treatment with reinforced lime. The samples treated with reinforced lime, with and without the addition of sodium stearate presented an inhomogeneous distribution of the neo-formed calcite crystals on the surface of the samples; the formed crystals present a different size and shape than the original marble crystals. The samples treated with the nano-dispersion of calcium hydroxide (A) presented an improved deposition covering the entire marble surface, the formation of calcite crystals is homogeneous and the formed calcite crystals present a better adhesion to the marble surface; furthermore, the addition of sodium stearate to the nano-dispersion (E) diminishes micro-cracking and at the same time increases the contact angle, thus also having a higher protective effect on the marble surface.

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