

DEGRADATION AND CONSERVATION OF MARBLE IN THE GREEK ROMAN HADRIANIC BATHS IN LEPTIS MAGNA, LIBYA

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Abstract

The Hadrianic Baths is one of the most important archaeological sites in Leptis Magna-Libya. It was built at the command of Emperor Hadrian in the early 2nd century CE; they represent some of the most lavish structures of Leptis Magna. It is unique in design and building technique. It was built of limestone, marble and brick. This paper mainly describes the deterioration of marble. The marble in the monuments can be classified into several types, based on its color, texture, chemical composition and the constituent mineral. The Hadrianic Baths is subjected to severe degradation, due to the climate, which is typically marine. This site suffered from different weathering forms, for example, disintegration of grains, pitting, chipping, frequent flaking, multiple-flaking, fissures and biodeterioration. These weathering forms were produced by many deterioration factors, such as moisture, salt weathering, biological and micro-biological factors, changes in temperature and wind erosion. The aim of this study is to characterize the building materials at the Hadrianic Baths, especially marble, and to evaluate the role of groundwater and sea weathering on the strength of the marble exposed to the coastline of the Mediterranean. Many samples were collected from limestone, marble, mortar, plaster and salts, for analysis and investigation. Several scientific techniques were used in the study of the morphology and texture. Those methods include microscopy, such as scanning electron microscopy (SEM), polarized light microscopy (PLM) and stereo microscopy. A qualitative identification of organic and inorganic chemical species was performed by using techniques such as energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD) and microbial investigation were also done. Our results indicated that the deterioration of marble was caused by the aggressive action of environmental agents. SEM observations indicated the occurrence of microcracks and particle aggregates in the samples. The study was also aimed to evaluate the efficiency of the various commercial silane-based and acrylic products in laboratory in order to recommend the protective treatment for the conservative treatment of the marble. To fulfill this goal a soaking characterization and accelerated ageing tests were performed. After artificial aging [included cycles of heating & cooling, salt weathering] proved that the [Rhdrosil or Tegvacon V] is the best material to consolidate the weakness of marble.

Keywords: Hadrianic Baths; Leptis Magna; marble; weathering; coastal; environment.

Introduction

The Leptis Magna monuments in Libya rank among the most important historical monuments of the world. They were discovered by Italian, American, British and Libyan archeologists during excavations performed since 1921. The Leptis Magna monuments were registered in the World Cultural Heritage List. The Hadrianic Baths are among the most famous

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monuments of Leptis Magna. Moreover, they are very large buildings in Africa. They were built at the command of Emperor Hadrian in the early 2nd century (126-127CE) and were changed at the command of Emperor Komodous (180-193 CE). The complex represents some of the most lavish structures in Leptis Magna [1]. Although they are not the largest of Roman baths, the Hadrianic Baths are a grand complex of buildings with reasonably varied and interesting internal volumes. Outermost was an open air swimming bath, with dressing rooms (*apodyteria*). The entire complex is symmetrical and it is possible that men and women could have bathed at the same time, separated from each other. Only the hot bath may have been closed for one group, surrounded on three sides by porticos and flanked by a pair of colonnaded halls. The columns surrounding the pool were made of granite, imported from Egypt, The hall between the two cold water baths, which measured about 20 x 18 m, was covered by cross-vaults in three sections; it was supported by eight heavy Corinthian columns made of cipollino (a type of green-white marble) that was imported from Carystus in Greece. Beyond that, on each side, there was a latrine with marble seats, on three walls. Four doors from the swimming bath opened onto a corridor surrounding the cold room (*frigidaria*) [2]. The cold room was a hall paved and paneled with marble, with a vaulted roof supported by eight columns. At each end of the hall arches opened onto cold plunge baths [3]. At the back of the hall a door opened onto the warm room with a large central bath and two smaller baths at the side. At either side was a super-heated sweating bath. Behind the warm room was a large barrel vaulted hot room with arched windows. Furnaces used for heating water are found outside the southern walls. Also note the several small rooms; these were changing cabinets, and the latrine with marble seats. Entrance to the baths are through the sports ground [4].

The Hadrianic Baths were built of different kinds of stone, such as black granite columns around the frigidarium plunge baths, native limestone blocks, excavated and cut to size, from local sources, were used from sources (at Wadi Zennad as well as Lebda itself). Brick is also used in some outside parts of the baths and also marble. The focus of this paper is on marble. The Hadrianic baths were the first buildings in the city to be built largely of marble, for both structure and ornaments. Several types of marble were described by authors, including the pink *brecia* marble columns surrounding the swimming bath (or natatio), the huge *cipollino* marble columns in the main frigidarium hall and another type of marble, mentioned as being used, which was a green *brecia*. Six types of marble are found in the Hadrianic baths: pink *brecia* marble, *cipollino* marble, green *brecia* marble, blue-gray *carrara* marble, yellow, yellowish-white *sienese* marble and white/black *creole* marble, according to the classification made by P. Kearey (2001) [5]. Marble was used as a building stone in Libya since the 2nd century CE, as decorative construction material, for sculptures, columns and pillars, for casing of walls and paving stones. It was a symbol of beauty in the grand buildings built by emperors [1]. Marble was used in both internal and external applications and is available in several colors and shapes. Marble is a metamorphic rock produced from limestone, by pressure and heat in the earth crust, due to geological processes. The pressures and temperatures, essential to produce marble, generally eliminate the fossils that exist in the initial rock; the texture of limestone is changed. Impurities in the limestone affect the marble mineral composition. Marble can be found in thick deposits, over wide areas that are relatively free of cracks and easy to quarry. It takes a high polish. The chief drawback of marble is its high susceptibility to disintegration under the action of acid rain. Marble is not a hard rock and tends to wear rapidly if used on floors and steps. Marble occurs in a wide range of colors due to the variety of minerals present in the marble, like clay, sand, and silt. Pure marble (calcite) is a brilliant white. Disseminated graphite in marble changes its color to gray or blackish-gray. Green tints result from the presence of chlorite. Pink and red marble owes its color to finely dispersed hematite or manganese carbonate. Yellowish or cream colored marble contains limonite. These colors may be evenly distributed or they may occur in bands. Marble is plentiful in western Anatolia, Italy, Greece and elsewhere in the Mediterranean area, so it was widely used in that region. During

the Roman Empire marble was exported all over the ancient world, such as to Libya. The aim of this work was to obtain more information about the specific forms of marble weathering developing under marine environmental conditions, to find the appropriate conservation and restoration treatments.

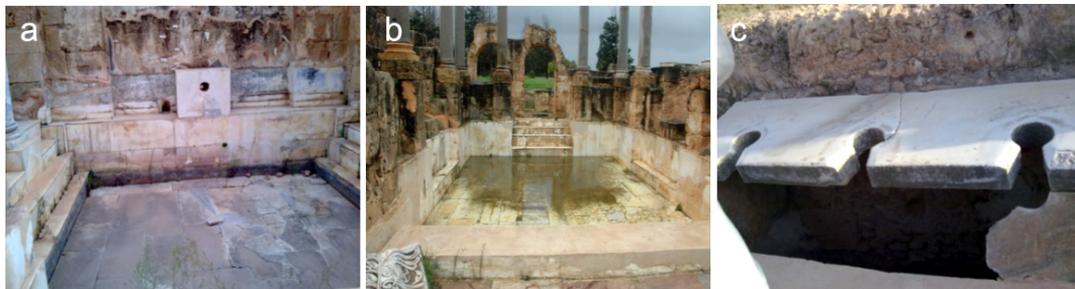


Fig. 1. The Hadrianic baths buildings: a - Entrance hall and swimming pool, b - Natatio room, c - The latrine with marble seats.

Local Climatic Conditions

The climate of this area is coastal. It is mostly semi-arid to arid, with short, rainy winter periods and long, hot and dry summer periods, with a significant diurnal variation of air temperature and air humidity. Our own microclimatic studies confirmed the high temperature variations at the surface of the monuments, with significant heating and cooling rates. Summers are hot and dry, while winters are mild and with scarce rains. During the spring, especially in April, along the coastline sometimes the Ghibli blows, a warm, dry wind that causes a sharp rise in temperature. The average July temperature is between 22°C and 29°C. In December temperatures dropped as low as 1°C, but the average remained between 9°C and 18°C. The average annual rainfall was less than 400 millimeters (15.7 in), and was very erratic (Fig. 2). However, the numerous cases of damage on columns, wall casing and paving stones made of marble indicated that the deterioration of building stones mainly depended on the climatic condition at Leptis Magna.

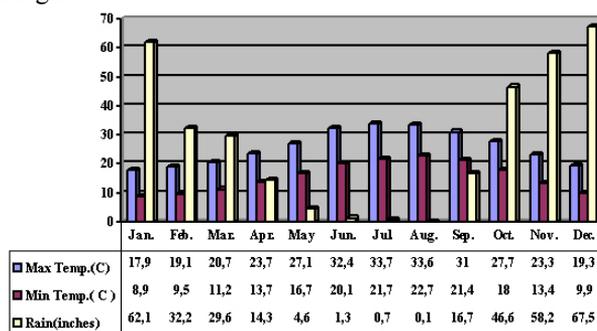


Fig. 2. The average temperature (high and low) and rain at Leptis Magna

Damaging factors

The weathering forms of the monuments manifest as loss of stone materials at the lower part of many walls, severe loss of stone material and considerable, recent marble casing deterioration (Fig. 3a and b). The mainly fine-grained marble of the baths suffered an increasing loss of stone material, the detachment of smaller stone elements from larger sized elements, flaking on the edges, and granular disintegration (Fig. 3c). Deterioration consists in a severe exfoliation of the marble pillars of the baths, cracks and chipping off pieces (Fig. 3d-f).The marble casing, slabs and columns show massive efflorescence, due to the surface salt

crystallization phenomena (Fig. 3g). That efflorescence was caused by moisture migration. Based on recent studies, a clear correlation between stone decay and combined water and salt effects can be postulated, proving that water and salt induce a weathering process that is the main and most harmful process. An intriguing phenomenon was noticed at the marble slabs of the latrine, which exhibited a tendency towards concave bowing (Fig. 3h). Microbiological colonization causing a dark-colored crust was noticed on the surface of columns and casing marble. Micro-organisms play an important and substantial role in all alteration processes that occur in the stone (Fig. 3i). Wrong restoration, represented by the improper use of Portland cement and Gypsum mortar to complete some missing parts and cracks of marble, plays an important role in the high concentration of various salts affecting the marble and causing disintegration. Those minerals dissolve in water and are re-crystallized on the wall surface, leading to many deterioration forms (Fig. 3b).

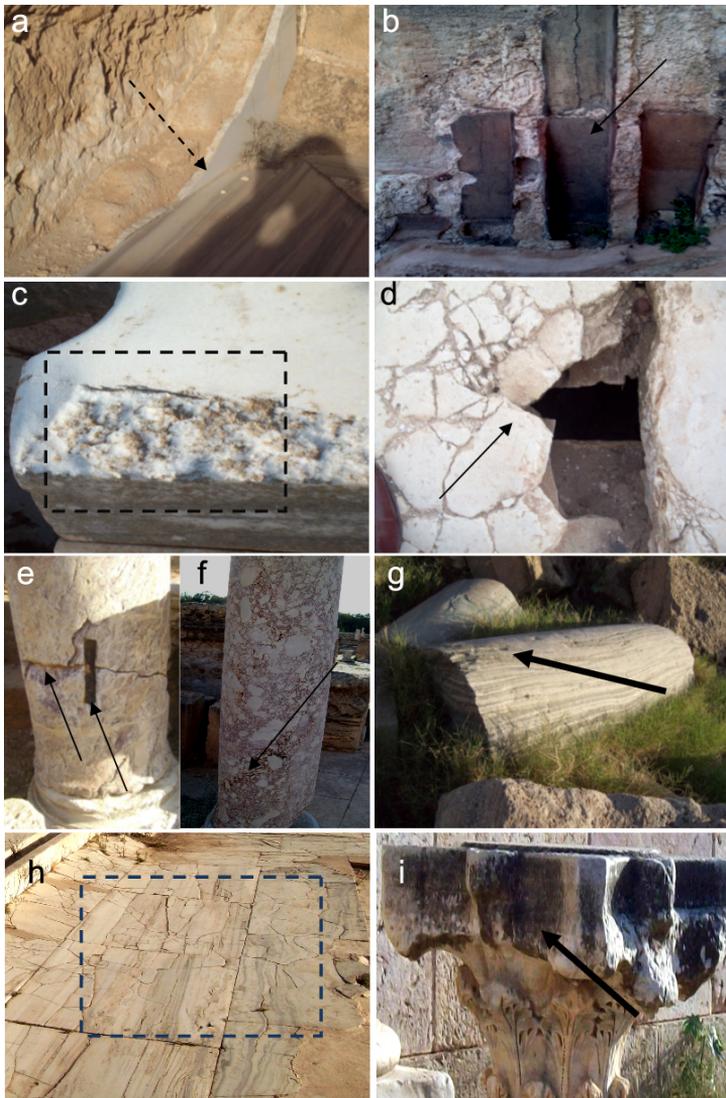


Fig. 3. General view and detailed images showing marble damage: a, b - detachment of marble casing; c - granular disintegration; d – cracks; e - exfoliation of the pillars marble; f - salt efflorescence; g - biological effect by plants; h - concave bowing i dark-colored crust

Materials and methods

The marble samples were collected from the wall casing, columns and the floor of the Hadrianic Baths. The samples represented the white, red, black, green and gray marble. They generally consisted of damaged layers. Selected samples were examined by means of several analytical methods.

Petrographic examination

The mineralogy characteristics, texture, cement materials and diagenetic features of marble samples were further examined by using a polarized optical microscope. Petrographic thin sections were prepared and optically analyzed by using a Leitz polarizing microscope.

L.O.M. Examination

The samples were observed by Stereo microscope on polished thin sections, by using a Leica DM 1000 stereoscopic microscope with a Leica EC3 camera. Optical microscopy (OM) was very useful for determining the different litho types present in monuments and for identifying the exact stratigraphy of the samples. It can provide information on the damaged layers, such as the sequence of layers, the particle size, color and texture of those layers.

Scanning electron microscope (SEM-EDX)

The surface features of the damaged layers was analyzed by Scanning electron microscopy (SEM), (SEM JEOL JSM 6400) coupled with an energy dispersive X-ray spectrometer (EDS), to reveal details of the diagenetic processes and micro-scale features in the marble. Small marble samples were coated with gold.

X-ray diffraction (XRD)

The identification of the mineral composition of the samples was made by X-ray diffraction patterns, using a Philips X-ray PW 1840 diffractometer. The patterns were run with Ni-filtered, Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at 30 kV and 10 mA. The scanning was limited from $2_{\theta} = 1$ to $2_{\theta} = 80^{\circ}$ range.

Results and discussions

Petrographic investigation

The examination of thin sections of the marble samples under plan polarized light microscope (PLM) revealed that: all marble samples are carbonate rocks consisting of both calcite and dolomite in rather variable proportions, with significant to moderate contents of quartz and orthoclase. There were very different textural features. All samples, from all sections, exhibited a more or less strong arrangement of the shape of anisotropic grains. The surface rocks show massive structures. The photographs show an increase in porosity and the samples showed more microcracks within thin sections. *The yellow and red marble* exhibits two sets of cleavage and were usually surrounded by small grains. Rare crystals of Quartz and orthoclase were observed. Contact metamorphism with high glare, relics of dolomite, fossil fragments and iron oxide were also noticed. *Black marble* revealed under the microscope a distinct banding, defined by a grey, white fine- medium and a coarse-grained layering. Occasionally local interbeds of thin, dark graphite-rich layers were observed. Two planar fabric elements or foliation could be differentiated; the bedding is recognizable by a change in the grain size, the graphite interbeds, as well as small, quartz grains arranged in layers. Most of the calcite crystals were granoblastic, with equidimensional shapes (pseudo-hexagonal) and different sizes.

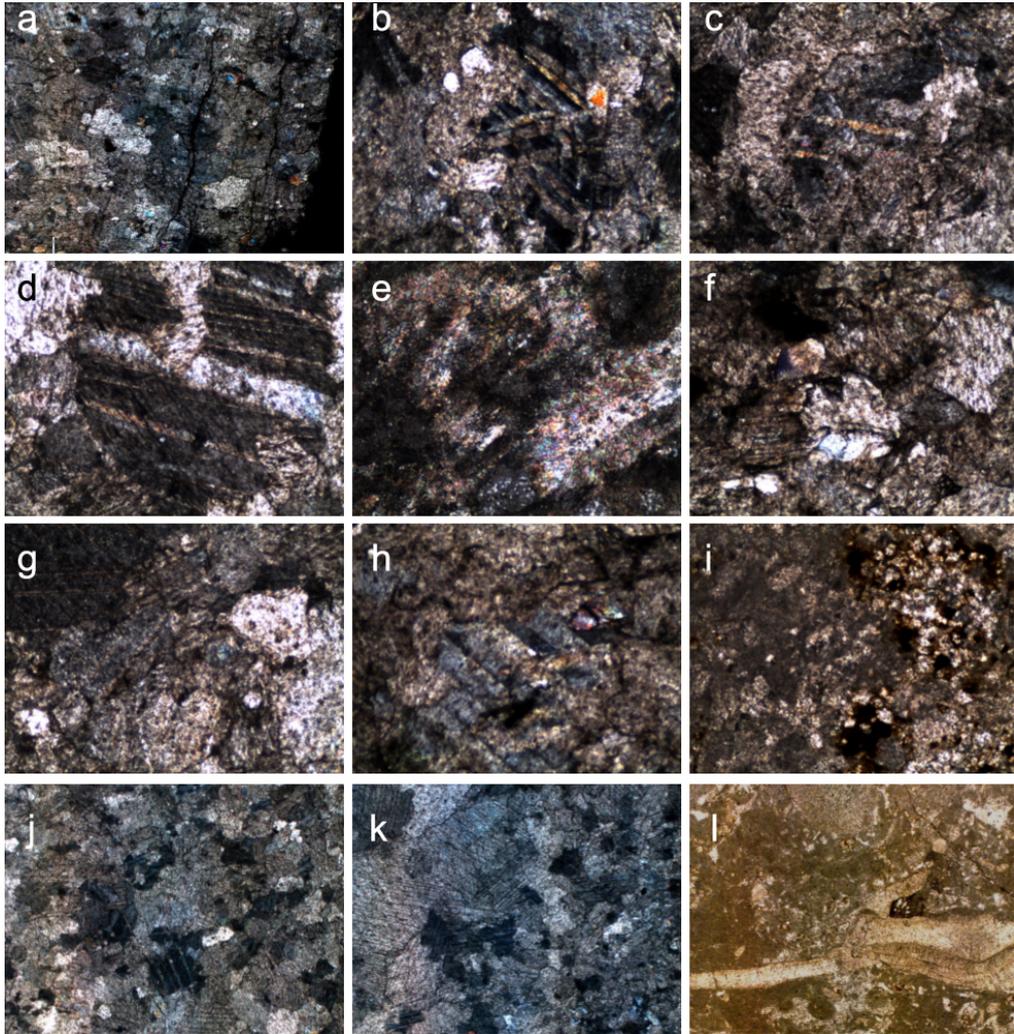


Fig. 4. The examination of the marble samples under polarized microscope shows (40X):
 a, b - cracks and microcracks; c, d, e - fine grains of calcite; f – cavities;
 g, h - clay minerals an grains of quartz; i - iron oxides;
 j, k - two sets of cleavage; l - fossil fragment

L.O.M. investigation

Optical microscopy revealed a typical polygonal granoblastic texture, with equidimensional shapes and grains of very various sizes. That texture clearly indicates a static recrystallization, in which the grain boundaries become straighter and grains increase in size, becoming hexagonal in shape. Those two processes finally produce a reduction of the grain boundary area and, therefore, a reduction of the total energy of the crystalline aggregate, (Fig. 5).

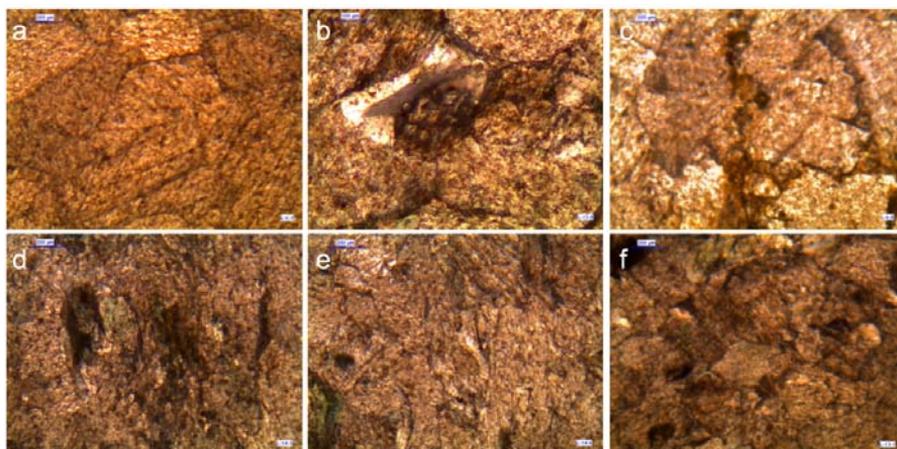


Fig. 5. Optical microphotographs of marble samples, showing their mineralogical composition and their texture of marble: a - morphology of white marble (200µm); b - green marble (100µm); c - laminated marble (200µm); d - yellow marble (200µm) ; e, f - red marble (200µm)

SEM-EDX Examination

The scanning electron microscope results confirm that a major deterioration is the abundance of soluble salts in the rock. SEM micrographs revealed that salt deposits on the marble surface caused several alterations, such as cracks, pores. Halite was identified in SEM micrographs as large prismatic grains (Fig. 6a-c) and there were losses of cohesion between grains. SEM photomicrographs showed disintegration between calcite crystals and micro exfoliation. The samples texture shows compact packing with isolated, localized cavities. The presence of such cavities and the discontinuation of the planar structure show that such regions are weak and can undergo preferential decay or losses (Fig. 6d-f).

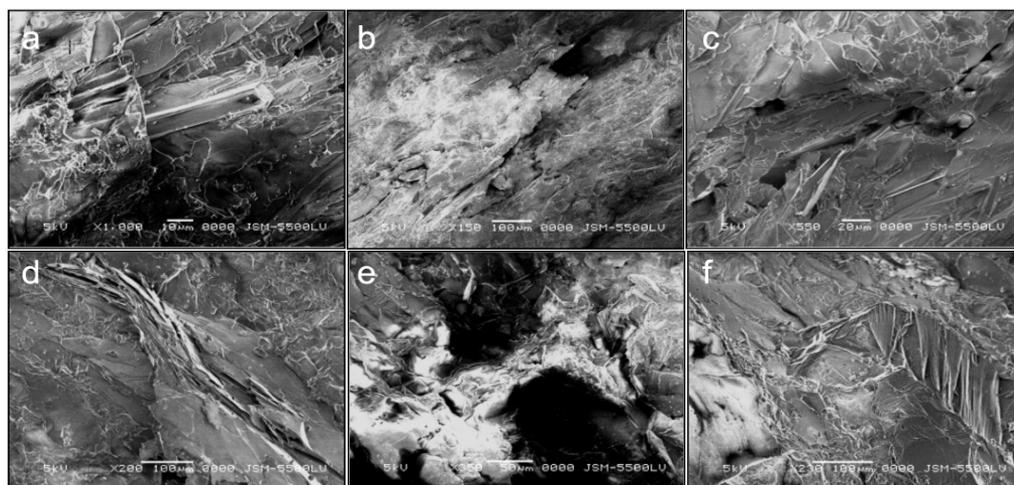


Fig. 6. SEM micrographs of deteriorated marble in the Hadrianic Baths: a and b - cracks, pitting and losses of cohesion between grains; c - different salt crystals such as halite in prismatic shape; d - micro exfoliation in calcite grains; e - dissolution of calcite crystals; f - a variety of cracking patterns in calcite grains.

EDX microanalysis of various marble samples listed in figure 6, detected that they had an almost pure carbonate composition, with low amounts of all the elements but Ca. The yellow marble had a slightly marly composition, with lower Ca (19.69%) values and a positive

correlation of silica with alumina and alkali amounts. Moreover, the marble was largely depleted of Fe (24.55%) and Sr. That distinguishing geochemical feature may be related to the different mineralogical compositions and the genetic environment of the materials. Some differences may also be observed in the white marble, which had a higher value of Ca (92.81%) and a lower one of Fe (1.27%). Pink marble had low amounts of sulfide and chloride (S and Cl), caused by weathering effects.

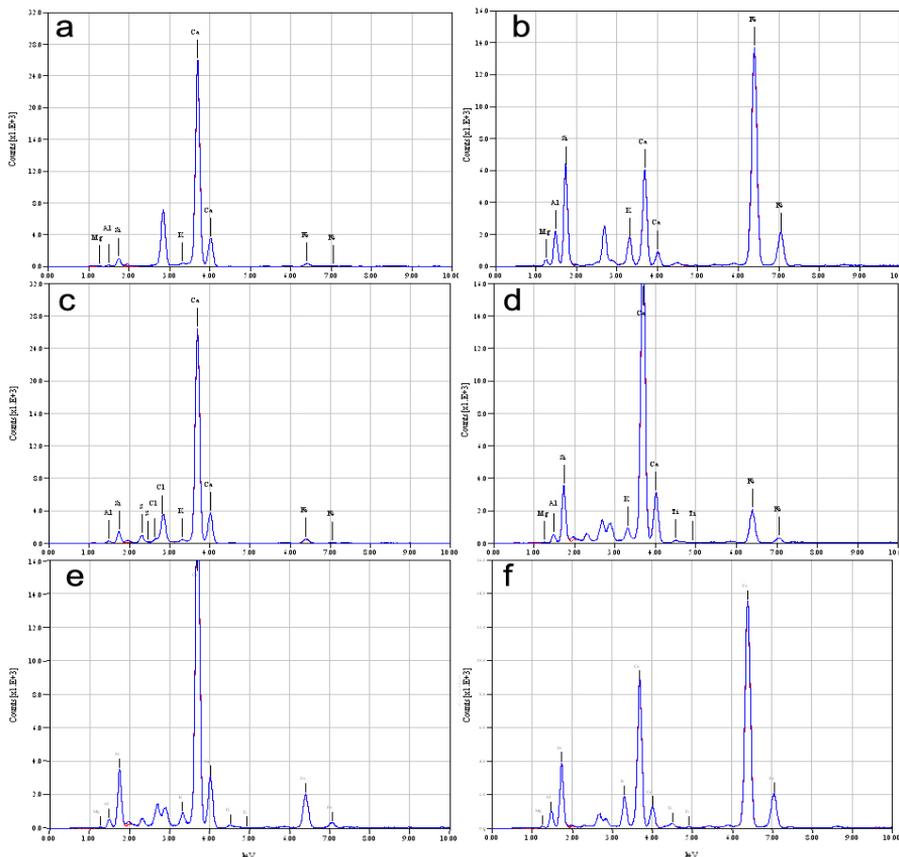


Fig. 7. EDX patterns of the marble samples from Hadriatic Baths: a - White marble, b - Yellow marble, c - Red marble, d - Black marble, e - Green marble, f – Grey marble.

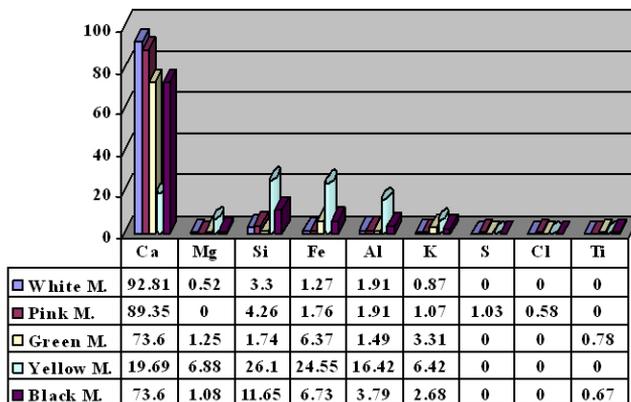


Fig. 8. EDX analytical results of affected marble samples at the Hadriatic Baths

X-Ray Diffraction analysis (XRD)

The XRD analysis of the various kinds of marble (the results are summarized in table 1) show that the *red marble* sample consists of calcite (CaCO_3), as a major component, in addition to dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) (Fig. 9c).

Black marble samples consist of calcite (CaCO_3) as a major component in addition to dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$), quartz SiO_2 , Fayalite Fe_2SiO_4 , and Forsterite Mg_2SiO_4 , (Fig. 9d).

Green marble samples consist of calcite (CaCO_3), as a major component, in addition to Ankerite ($\text{Fe, Mg} \text{CO}_3$), Microcline KAlSi_3O_8 , Forsterite Mg_2SiO_4 , Nepheline $\text{NaAlSi}_3\text{O}_8$ (Fig. 9e).

Yellow marble samples consist of calcite (CaCO_3), as a major component, in addition to quartz SiO_2 , Kaolinite, Iron oxide, Antigonite (Fig. 9b).

Red marble sample consists of calcite (CaCO_3) as a major component in addition to quartz, (Fig. 9c).

White marble samples consist of calcite (CaCO_3), as a major component, in addition to quartz SiO_2 , silicon oxide, gypsum and Nepheline ($\text{NaAlSi}_3\text{O}_8$)

Grey marble samples consist of calcite (CaCO_3), as a major component, in addition to dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) (Fig. 9f).

Laminated marble samples consist of calcite (CaCO_3), as a major component, in addition to dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$).

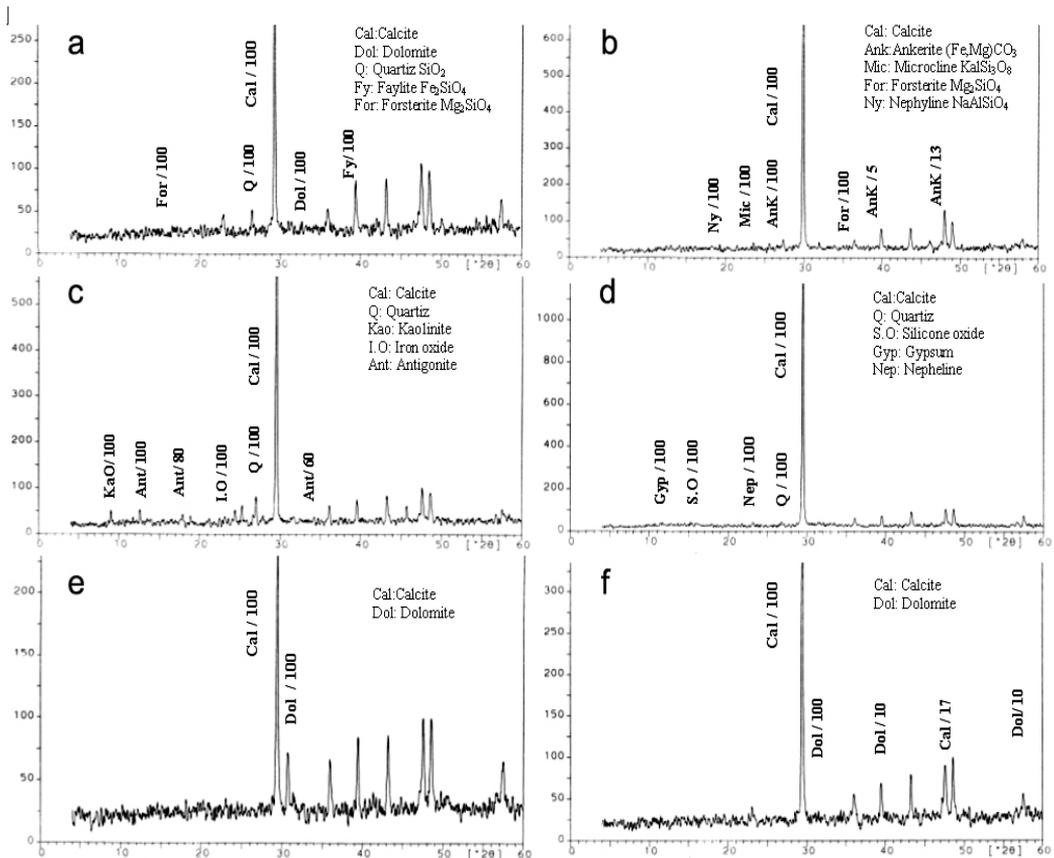


Fig. 9. XRD pattern of marble samples from Hadrianic Baths: a - black marble, b - green marble, c - yellow marble, d - white marble, e - grey marble, f - red marble.

Table 1. X-ray diffraction analysis results

Sample	Calcite	Dolomite	Quartz	Kaolinite	Microcline	Forsterite	Ankerite	Nephline	Faylite	Gypsum	Iron oxide
White marble	***		**					*		*	
Red marble	***	**									
Green marble	***				*	*	*	*			
Grey marble	***	*									
Black marble	***	*	*			*	*		*		
Yellow marble	***		*	*			*				**

Treatment and conservation suggestions

Our field investigations and lab analyses indicated that the marble at Leptis Magna need different treatments and conservation processes, which include consolidation and water repellent treatments, the removal of plants, the removal and extraction of salts and stone fillings.

Consolidation

For this study, four products of conservation were tested: Rhodorsil 224 (alkyl-alkoxyl-siloxane) diluted in trichloroethylene, Wacker OH100 (Wacker-silicone-OH, non hydrophobic product containing tetraethoxysilane and oligomers, ketonic solvent), Tegovacon V, Ethyl silicate: (TEOS) tetraethox silane.

The application of the consolidant to the marble samples

The study was aimed to evaluate the efficiency of the various waterproofing products in the laboratory, in order to recommend the best protective treatment for the conservation of marble. The materials for our tests were taken from the Zafarana area. The site is located next to the quarry through Zafarana marble paved through the Suez Ras Gharib, Jebel Tlmit, which is located in the far northeast of the East of El_Galala plateau and about 125 km away from Suez and about 90 km away from Ras Gharib. It was white marble with some grayish banding. At first 50×50×30 cm blocks were cut, from which we cut specimens measuring 5×5×15 cm, cubic samples of 3.5×3.5×3.5cm and slabs (7×7×3.5 thickness) (Fig. 10).



Fig. 10. The marble samples before ant treatment.

Those samples were submitted to artificial weathering cycles (AWC). The specimens of marble were subjected to cycles of saline baths (1:1) of 20 % Na₂SO₄ and 20 % NaCl and to heating (105°C). The samples spent 16 h in the saline bath, then 6 in the oven, then 2h at room temperature and were then placed in a saline bath for 6 h. The treatment consisted of 15 cycles of AWC with a total time of 360 h. The aged samples were washed under tap water. There was

a perceivable change in the appearance of samples. There was a substantial decrease in physical and mechanical properties as shown in tables 2, 3 and 4.

Table 2. The main physical characteristics of studied marble before and after artificial weathering

Property	Without soundness	After soundness by saline bath and heating
Bulk Density [gm/cm ³]	2.14	1.92
Water absorption [%]	7.2	12.35
Porosity[%]	9.42	12.34
Compressive strength [gm/cm ²]	167	165

Table 3. The main mechanical characteristics of studied marble before artificial weathering

Samples	Size (cm)			Weight (gm)	Compressive strength (k/n)	Abrasive	Bending
M1	3.3	3.2	3.4	85.13	45.16		
M2	16	3.3	3	413			2.090
M3	7.1	7	3.4			21.40	

Table 4. The main mechanical characteristics of studied marble after artificial weathering

Samples	Size (cm)			Weight (gm)	Compressive strength (k/n)	Abrasive	Bending
M1	3.3	3.2	3.4	81.13	32.71		
M2	16	3.3	3	410			0.816
M3	7.1	7	3.4			24.64	

The aged samples treated with consolidant materials spent 22h, then 2h at room temperature. The same treatment was repeated for 10 cycles. After 21 days of indoor curing at room temperature, a visual inspection was performed to evaluate any alteration of the surface appearance (color and gloss). According to the visual appearance, the best products were Tegovacon and Rhdrosil. The Wacker OH changed the color of the marble significantly, to an unacceptable level.

In order to obtain the most suitable polymer for consolidation, resistant to different weathering factors, the experimental conditions used for the purpose of artificial weathering were far more severe than natural conditions. The test was carried out by wet-dry cycles and salt crystallization weathering (ASTM Designation C88 – 56 T). The results were determined after 15 cycles. Physical and mechanical properties were determined as shown in (Fig. 11).

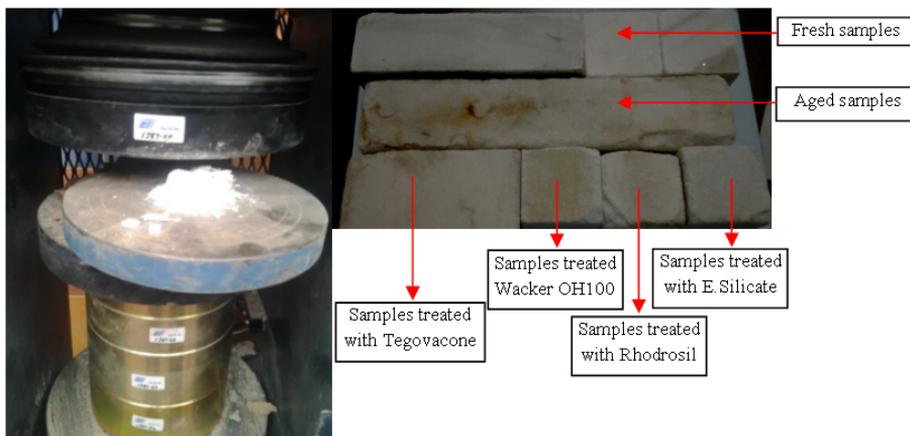


Fig. 11. The test of compressive strength b marble samples after ageing, before aging, after treatment with consolidant materials

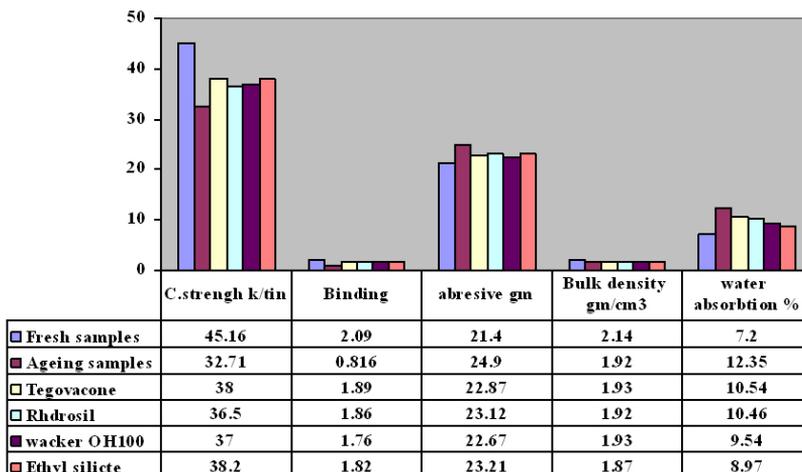


Fig. 12. The physical-mechanical proprieties of marble after treatment with consolidant materials

Vegetation removal

Leptis Magna area, including the Hadrianec baths, suffers from the growth of wild and sea grass, because of the high level of groundwater leaking from the sea to the area. Researches suggested two methods for the treatment of this problem. Mechanical removal of roots and rhizomes (a plant-like stem of roots) of the wild *Phragmites Australis* and *Imperata cylindrical*, plants that are widespread in the region. The correct treatment of the problem of wild grass begins by treating the cause of growth - a high level of ground water. Chemical removal of *Alhagi* and *Tamarix nilotica*, by using chemical pesticides, was one of the most effective methods. The chemical removal was more appropriate because it destroyed the weeds completely, without re-germination. The use of pesticides systematically affects plants in all parts. The pesticides were the ones previously tested by the laboratories of research at the Supreme Council of Antiquities, including the pesticide Glyphosate, its trade name being Round Up (it is a group of acid derivatives of Glycine) and the pesticide Fuluazifop-p-butyl, its trade name being Fusilade, used for the treatment of cracks and crevices, gaps and joints in the marble casing, so as to remove the seeds.

Discussion

Our field investigations and lab analyses revealed that the marble decay at the Hadrianic Baths was caused by different actions that deteriorate the marble. The baths region is exposed to marine climate, so the Mediterranean Sea acts as the main source of groundwater and plays an important role in the deterioration process.

The microscopic examination of several thin sections revealed that marble grains were affected by saline water, which produced micro fractures and cracks (Fig. 6), resulted mainly from salt crystallization, which occurred during the repeated drying and wetting phases. SEM diagnosis indicated the presence of Halite between the grains of marble, in two states: prismatic crystals and cubic ones. Salt crystallization is one of the major threats to historic monuments located in marine environments, particularly for historic buildings that stood for centuries at the edge of the sea, such as the complex at Leptis. The presence of sodium chloride in the sea spray and fogs caused their severe deterioration and they were also affected by sodium chloride crystallization, since large amounts of this salt can accumulate [6, 7]. One of the main reasons for the grain cohesion of marble was soluble salt, such as sodium chloride, which may penetrate deeply and cause the expansion of the pre-existing transgranular cracks, due to a volume

increase during the process of crystallization, when the solvent evaporates [8]. In coastal environments, especially during windy and/or stormy conditions, the wetting/drying process may induce a progressive adsorption of water molecules in the grains of marble surfaces and this may cause a decrease in strength. Also, it leads to the development and opening of fractures (resulting from stress, fatigue, wetting and drying, freeze–defreeze actions) and the deterioration of the rock materials, as a result of the infiltration of water (resulting in dissolution, chemical alteration, physical breakdown through freeze–defreezing, or salt crystallization) [9].

The microscopic examination of several samples revealed that marble grains were affected by mechanical processes which produced micro fractures, exfoliation and cracks (Fig. 4, 6). Temperature and moisture conditions are key parameters in mechanical weathering processes of building stone. Marble as building material, as well as in its natural environment; shows complex weathering phenomena. According to several authors, the most important weathering factor for marble is based on the highly anisotropic thermal dilatation coefficient of calcite [10]. Structural anisotropy is more enhanced by the shape of the calcite crystals and their texture [11]. The irregular expansion and contraction of calcite crystals during heating and cooling, causes a detachment of the grains and eventually the disintegration of the structure. The final stage of this weathering is frequently characterized by a sugar like disintegration of marble. Hadrianic Baths feature this classical tendency, called *sugaring* (Fig. 3c) and marble can be reduced to a monocrystalline calcite powder with the pressure of a finger. This feature is common to several other documented cases of structural deficiencies in marble constructions [12].

An intriguing phenomenon was noticed in the marble slabs of the latrine, which exhibited a tendency towards *concave bowing*, (Fig. 3h). Many studies have tried to explain that phenomenon. *C. Widhalm et al.* [13] performed experiments that proved that permanent elongation can be produced by uniformly heating marble slabs. The bowing phenomenon, however, could only be partially reproduced. *E.M. Winkler* [14] stresses the need for moisture in order for marble slabs to buckle. Calcitic marble is more sensitive to thermal expansion than dolomitic, because calcite crystals, when heated, show a positive expansion coefficient on their c-axis, and a negative one perpendicular to it [8-14]. This anisotropic behavior of the calcite grains leads to changes in the grain shapes after heating, which favor an increase of the micro fractures until a decohesion of the stone occurs. The marble bowing of the slabs may not only be caused by the thermal variations in seasonal changes. We can also suppose that there were several other causes: moisture, freezing and thawing, thermal gradients, chemical aggression, etc., acting together [8].

Mineralogical investigations were done by XRD (Fig. 8 and table 1) revealing that the main mineral composition of the marble was Calcite and the accessory minerals were quartz, dolomite, faylite, nepheline, microcline, ankerite and kaolinite. *Forsterite* (Mg_2SiO_4) is the magnesium rich end-member of the olivine solid solution series. It is associated with igneous and metamorphic rocks and has also been found in meteorites [15]. *Fayalite* (Fe_2SiO_4) is the iron-rich end-member of the olivine solid-solution series. In common with all minerals in the olivine group, it crystallizes in the orthorhombic system, Fayalite is stable with quartz at low pressures, whereas more magnesian olivine is not, because of the reaction olivine + quartz = orthopyroxene. Fayalite can also react with oxygen to produce magnetite + quartz [16]. *Nepheline* ($NaAlSi_3O_8$) also called nephelinite, or eleolite, the most common feldspathoid mineral, is an aluminosilicate of sodium and potassium $[(Na,K)AlSi_3O_8]$. *Microcline* ($KAlSi_3O_8$) is an important igneous rock-forming tectosilicate mineral. It is a potassium-rich alkali feldspar. Microcline typically contains minor amounts of sodium. It is common in granite and pegmatites. Microcline forms during slow cooling of orthoclase; it is more stable at lower temperatures than orthoclase [17]. *Ankerite* $(Fe,Mg)CO_3$, is a calcium, iron, magnesium, manganese carbonate mineral of the group of rhombohedral carbonates with formula:

$\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$. In composition it is closely related to dolomite, but differs from this in having magnesium replaced by varying amounts of iron and manganese. Ankerite occurs with siderite in deposits of iron-ore. It is one of the minerals of the dolomite-siderite series, to which the terms brown-spar, pearl-spar and bitter-spar have been historically loosely applied. Ankerite can result from hydrothermal or direct groundwater precipitation. It can also be the result of metamorphic recrystallization of iron-rich sedimentary rocks. It is often found as a gangue mineral associated with gold and a variety of sulfide minerals in ore deposits, Iron oxide (pyrite), Antigonite, Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. *Kaolinite* is a clay mineral produced by the chemical weathering of aluminum silicate minerals [18]. Clay minerals including Kaolinite form by the weathering or hydrothermal alteration of feldspars, thus occur in weathering aluminum silicates fine-grained elastic metamorphic rocks [19]. This declares the great problem of hydric expansion and shrinkage due to absorption and loss of water. Hydric expansion is one of the most important reasons for deterioration of marble. The aggregation/disaggregation or swelling/ shrinking of the clay particles occurs when these particles interact with water causing a whole series of identifiable pathologies in building stone. The swelling types of clay minerals were linked with their crystallographic structure and bonding properties, especially in the case of interlayer spaces [20]. Osmotic swelling occurs for all clay mineral types in response to an electrolyte concentration increase in the double diffuse layer on clay mineral surfaces. Different clays react differently to hydric expansion, while the textural anisotropy of clay bearing stones appears to play a critical role on swelling- shrinking related damage [21].

EDX data presented in figure 8 revealed that, the marble consist of essentially calcium (Ca), silicon (Si), sulfur (S), chlorine (Cl), sodium (Na), aluminum (Al), iron (Fe), magnesium (Mg), potassium (K) and titanium (Ti). The sulphate and chlorine ions are attributed to the gypsum and halite salts formed within the marble. The sources of sulfate ions may be ascribe to air pollution. Environmental pollution in urban Leptis Magna causes decay of historic marble at the Baths. The acid constituents (CO_2 , NO_x , SO_x and their derivatives) acting on marble surfaces have caused irremedial damage to the marble. Sulfur dioxide has a particularly harmful effect. It reacts with moisture, oxygen and calcium carbonate, the product of this sulfatation process is calcium sulfate dehydrate (gypsum) [22] which appear as crusts on the stone surfaces. These sulfates may be dissolved by rainwater or may be precipitated within the pores of the stone, where, specific volume of calcium sulfate is higher than of that of calcium carbonate [23] upon recrystallization, they can exert tremendous stresses on the pore walls due to an increase in volume causing stone damage, manifested as exfoliation [24].

Plants are the main biological deterioration factors of the marble at the baths. The deterioration caused by plants is both mechanical and chemical. The roots grow mainly in the mortar between the marble blocks or the marble layers covering the walls that is in the areas of least resistance. But the more compact areas can also be colonized when a reduction in the cohesion of the materials occurs as a result of other physical and chemical factors of deterioration. The pressure exercised by the growth and radial thickening of roots can cause serious damage to the marble [25]. So the research recommended using mechanical methods to remove the wild grass from the Hadrianic bathes and using the chemical pesticides is the most appropriate because it destroys the weeds completely without re-germination.

The microscopic observations proved that, the weakness of the internal structure of marble and its granular disintegration due to the loss of surface material links between the grains, due to the action of water and salts, decreasing stone durability. So different water-repellent consolidants were determined. Water-repellent coatings are formulated to be vapor permeable or *breathable* [26]. They do not seal the surface completely to water vapor so it can enter the masonry wall as well as leave the wall. Most water-repellent coatings are water-based and formulated from modified siloxanes, silanes and other alkoxysilanes [27]. Some of these products are shipped from the factory ready to use. Our study of the physical and mechanical properties of the consolidated specimens of marble, with four consolidation materials, after

artificial aging, (including cycles of heating & cooling, salt weathering) proved that the *Rhdrosil* or *Tegvacon V* is the best material to consolidate marble.

Conclusions

The present work revealed that the marble of Hadrianic Baths suffers from different deterioration phenomena, such as missing parts, erosion of stone surfaces, different types of cracks, disintegration of many parts, crystallization of salts and dirt. The deterioration factors were different sources of moisture, salts, wind erosion and changes in temperature and moisture. Moreover, there were some other chemical damages and forms, especially those related to saturation conditions, such as split off thin overlying layers and the formation of grooves, resulted from water accumulation. All of these deterioration forms were followed by different physical and mechanical forms, which will be a topic for further research. Our lab study indicated it was recommended to use Rhedrosil and Tegovacon V for consolidation.

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