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A Comparative Study for Evaluation of Remedial Efficiency of Phosphate-BASED Treatment and TEOS-BASED Composites in Strengthening Monumental Limestone, A Case Study.

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Abstract

In the last three decades, Ethyl silicate is currently the most widely used among stone consolidates; nevertheless, its reduced efficacy on calcite substrates, where it exhibits some drawbacks that hinder their performance in terms of either mechanical efficacy, compatibility with the substrate and/or durability, make the research for alternative consolidates for carbonate stones necessary. This paper deals with a comparative study between TEOS-based treatment and phosphate-based treatment for limestone consolidation. The idea of using phosphate-based treatments is forming calcium phosphates (ideally hydroxyapatite) as the reaction product between the substrate and an aqueous solution of a phosphate salt that the stone is treated with. The experimental study was conducted on limestone samples from Saqqara archaeological area, Egypt. Some tests were performed for studying the behavior of the consolidates used. The main aim of these tests is to estimate the consolidates efficiency and investigate the changes of physio-mechanical properties of the studied samples before and after consolidation. The obtained results showed that the hydroxyapatite treatment exhibits a good efficacy in terms of mechanical properties and, compared to treatment based on TEOS, it causes less pronounced alterations in open porosity and water transport properties. This makes the new treatment a potentially valid alternative to treatment based on Ethyl silicate, especially in those situations where the possible presence of water behind the consolidated layer (e.g. in case of rising damp, condensation or infiltration) might threaten the durability of the consolidation intervention.

Keywords

Ethyl silicate - Diammonium hydrogen phosphate - consolidates - Wacker BS OH 100 - compressive strength.

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1. Introduction

As of their extended use in historical buildings and architecture, the consolidation of weathered carbonate stones, such as limestone and marbles, is a key goal in cultural heritage conservation and many experimental studies have been aimed at improving the existing consolidating treatments and developing materials (micro and nano) compatible with natural and artificial stone [1].

Consolidants must fulfill many requirements not only in terms of consolidating efficacy (ability to recover the cohesion of the decayed material), but also in terms of compatibility with the substrate (i.e. should not cause any damage to the substrate or adjacent material) and, at the same time, be durable. From this point of view, inorganic consolidants seem quite attractive, as they are generally stable and durable [2].

Stone consolidation needs careful designing and preliminary testing, as it is basically an irreversible intervention in most cases [3-5]. Moreover, consolidation might even result in an acceleration of materials decay, if unsuitable materials or treatment conditions are selected. For these reasons, the study of stone consolidants is of primary importance [6].

Consolidants based on alkoxysilane precursors are commonly employed in the preservation of stonework [7]. The alkoxysilanes and alkyl alkoxysilanes, or “silanes” for short, have undoubtedly been the most widely used stone consolidants over the past thirty years [8]. An advantage of these materials over organic polymers is that they are applied as low molecular weight monomers or oligomers that polymerize to form consolidants inside the stone. The implicitly low viscosities of the starting materials greatly improve penetration depths. In this study, one of the simplest alkoxysilanes employed in commercial formulations was selected, tetra-ethoxysilane or tetraethyl orthosilicate (TEOS), also known as ethyl silicate [7,9].

Although ethyl silicate is currently the most widely used among stone consolidants in the past decades; nevertheless, its reduced efficacy on calcitic substrates, where it exhibits some drawbacks that hinder their performance in terms of either mechanical efficacy, compatibility with the substrate and/or durability, make the research for alternative consolidants for carbonate stones necessary [10]. In the recent paper, two consolidants used in limestone consolidation, one is organic based on TEOS, and the second is inorganic which is an aqueous solution of diammonium hydrogen phosphate DAP, $(NH_4)_2HPO_4$ were used and applied to limestone samples from Saqqara archaeological area, Egypt to compare between them as two consolidants for treatment of monumental limestone under study.

The case study in this current paper is an inscribed funerary limestone stela (cavernous engraving) which was discovered during excavations in the site of the New Kingdom in Saqqara, Giza, in 2014. The stela was very fragile and suffered from bleeding of stone once being touched, which led it to be initially cleaned of dust and dirt and was kept in Saqqara stores in order to save the remained inscriptions and do some experiments to decide the best consolidant to be applied.

It was discovered during the excavations in 2014. The stela is a rectangular stone painting with a circular surface from the top. It is 1.02 x 0.51 x 0.14m, and it was made by cavernous engraving style , Fig (1). Its inscriptions are divided into three rows. The upper row shows a man and woman in front of the god of death; the middle row shows three people carrying offerings in front of the owner of the tomb and his wife; the last row shows two men and three women carrying oblations. Their clothing probably dates back to the New Kingdom.

Fig. (1) shows the inscribed funerary stela.

Technical Analysis of the funerary stela:

The Upper Section, Fig (2):

From an artistic point of view, the artist balanced this section by increasing the size of the god of the dead on the left side, while the two people were painted in a smaller size. He used lines of all kinds to border the characters. For example, curved lines were used to draw heads, arms, legs and some parts of clothes, while straight lines were used to draw sticks, chairs and some parts of the clothes. As for the rhythm, it was achieved in the repetition of some parallel or radiant lines or the movement of the arms of the two people standing in front of the god of death.

Fig. (2) The upper section of stela.

The Middle Section, Fig. (3):

The artist balanced this section by making one of the characters stand in the middle of the space. On the left, two people are sitting; and on the right, two characters are in a standing position. The artist used straight and curved lines. As for the rhythm, it was achieved through the repetition of the movement of the hands of the two people on the right side of this section, as well as the two Lotus flowers with their sticks. Moreover, there are a few accelerated rhythms generated through the broken straight lines and the geometric spaces confined between them, which seem to be increased in the direction from left to right on the chair on the left.

Fig. (3) The Middle Section.

The Lower Section, Fig. (4):

The artist balanced this section by distributing characters in approximately equal distances of the allocated space, along with some decorations and symbols above this space. In addition, the artist varied in the use of both straight and curved lines in drawing people, clothes and symbols. As for the artistic rhythm, it was achieved by repeating the movement of the hands in all the characters and hair blocks, and the size and clothing of the three characters on the right of the part. The same applies to the shape and lines of clothing and the movement of the legs in the two characters to the left of the part.

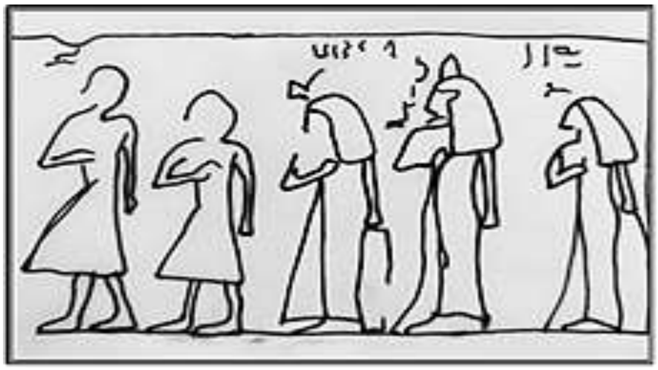

Fig. (4) The Lower Section.

Generally, for some reasons, the owner of the cemetery or his relatives hired a non-professional artist, or the artist did not pay much attention to draw this stela. This appears through the weak shaky lines with which he painted the characters and some other elements. There is also an inconsistency in the human proportions in drawing some parts such as arms, legs and feet, as well as in some characters he overlooked adding some facial details or necklaces and decorations. The stone stela had many aspects of deterioration, such as the accumulation of dirt, dust and dark spots, gaps, crusts on the surface layer, fragment of large parts of it, and the loss of colors, Fig (5).

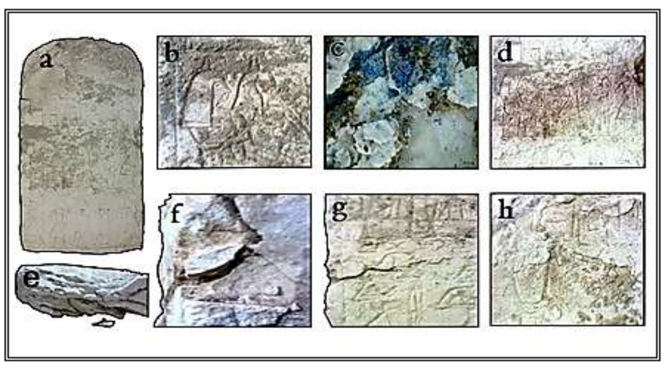

Fig. (5) shows the deterioration phenomena of the funerary stela; a. the stela covered by dust and muddy grimes, b.accumulation of dust, c. crusts on the surface layer, d. losing of color, e. gabs and limestone bleeding, f., g. cracks, h. dark spots.

2- Materials

Studied samples

Representative limestone samples were carefully selected from the archaeological area. Study samples used were cut on cubes forms of 5×5×5 cm. Untreated specimens were also tested for reference purposes.

Consolidants

The first consolidant is an aqueous solution of diammonium hydrogen phosphate (DAP, (NH4)2HPO4), Fig. (6). DAP is a novel inorganic consolidant has recently been proposed for the treatment of carbonate stones used in architectural and cultural heritage. The core idea is that stone can be consolidated thanks to the formation of hydroxyapatite [HAP (Ca5(PO4)3(OH), usually written as Ca10(PO4)6(OH)2] inside pores and micro-cracks between grains. According to the following equation, HAP can be formed from the reaction between Ca2+ ions deriving either from partial dissolution of the stone or externally added and PO43- ions coming from the aqueous solution of diammonium hydrogen phosphate (DAP) [11-17]: $5\ Ca_2+ + 3\ PO_4^{3}- + OH^- \rightarrow Ca_5(PO_4)^3(OH)$

The second consolidant is TEOS: Tetra-ethoxysilane or tetraethyl orthosilicate, also known as ethyl silicate, Fig. (6).

Fig. (6). Appearance of the two consolidants.

3- Methods and techniques

Different analytical and investigation methods were used to study the experimental samples:

Polarizing microscope

Petrographical investigation conducted for the studied samples according to [19] using the polarizing microscope (Olympus BX50, Japan) associated with computer software imaging system called (analysis) in the geology and petrographical investigation laboratory of National Housing and Building Research Centre (HBRC), Cairo. It aims to identify the texture, fabric and micro-structure of the samples under investigation. On the other hand, it is also used to identify the presence or absence of weathered or altered minerals and its effect on the properties of the stone [20].

X-ray diffraction (mineralogical analysis)

X-ray diffraction was used for identification of the mineralogical composition of the studies samples [21], using X-ray model X' Pert Pro Phillips MPD PW 3050/60 X-ray diffractometer in the XRD lab of the HBRC.

Scanning electron microscope (SEM)

Scanning electron microscope, JEOL JSM-5400LV at Assiut University, was used to determine the morphology of the particles and voids [21] and to detect the consolidants penetration efficiency for the treated samples to determine the best of these substances in penetration [20].

Moreover, the physico-mechanical properties (bulk density, water absorption, apparent porosity, and compressive strength) were measured for the studied samples based on documented standard typical methods [22-24].

Treatment process

The experimental study was carried out on some samples of limestone blocks collected from Saqqara archaeological area. The samples were prepared on cubes (5×5×5cm) and they were used as a target for the consolidation process using an aqueous solution of diammonium hydrogen phosphate, DAP (3.0 M) and TEOS. According to literatures [26-28], the samples were cleaned perfectly to remove the dust. Then they were dried in the oven at 60°C. Consolidants were applied via a capillary absorption with covering the path by glass cover to minimize solvent evaporation, Fig. (7a).

As for the phosphate treatment, treatment with DAP solution alone however has two drawbacks: (i) not only HAP, but also other metastable calcium phosphate phases are formed; (ii) small unreacted phosphate fractions remain in the stone. To overcome these drawbacks, different strategies have been proposed, such as providing additional calcium sources, controlling the DAP solution pH and applying a limewater poultice as a second step [11].

So was the second step of the treatment, which consisted of applying a limewater poultice onto the treated surface of the samples (a sheet of filter paper being inserted between the sample and the poultice to avoid sticking). The limewater poultice was prepared using dry cellulose pulp and limewater, i.e. a saturated solution of calcium hydroxide and de-ionized water. The weight ratio of limewater to dry cellulose pulp was 6:1. After poultice application, samples were wrapped in a plastic film for 24 hours (to avoid limewater evaporation), , Fig. (7b). Afterwards, the samples were unwrapped and the poultice was left to dry in contact with the samples until constant weight (about 4-5 days). The poultice was then removed, the samples were rinsed with de-ionized water and finally left to dry until constant weight (about 2-3 days) [11-13,25-31] .

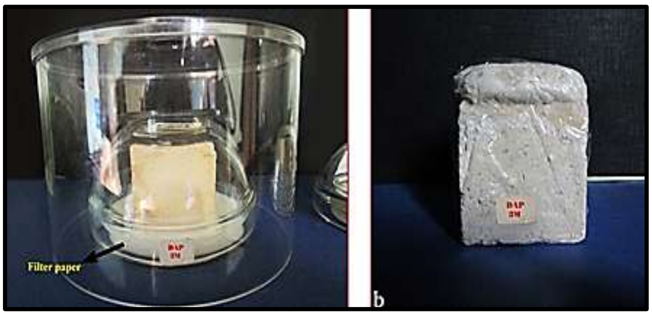

Fig. 7. a) Limestone sample placed in aqueous solution of DAP (3.0 M) with careful covering process; b) applying a limewater poultice onto the treated sample, and wrap the sample in plastic film.

On the other hand, treated samples by TEOS were left to cure for 4 weeks (as recommended by commercial TEOS products technical datasheets) in laboratory room conditions (T = 20 ± 2°C, RH = 50 ± 5%).

4-Results

Polarizing microscope investigations

The result of the investigation indicated that the studied limestone was Packstone microfacies (Kendall, 2005 after Dunhum, 1962). As it comprises over 50% allochems (interaclast and bioclasts) grains such as foraminifera ranging in size from microsparitic to sparitic, i.e. from 4m to 15 m and more than 15 m, respectively. These grains embedded in a micritic matrix represent over 2/3 of these facies with less sparry calcite cement, so they can be classified as Packed biomicrite facies based on (Kendall, 2005 after Folk, 1959), Fig. 8.

Mic: Micritic calite , Num: Nummlites, Sp:Sparite, F:Fossils.

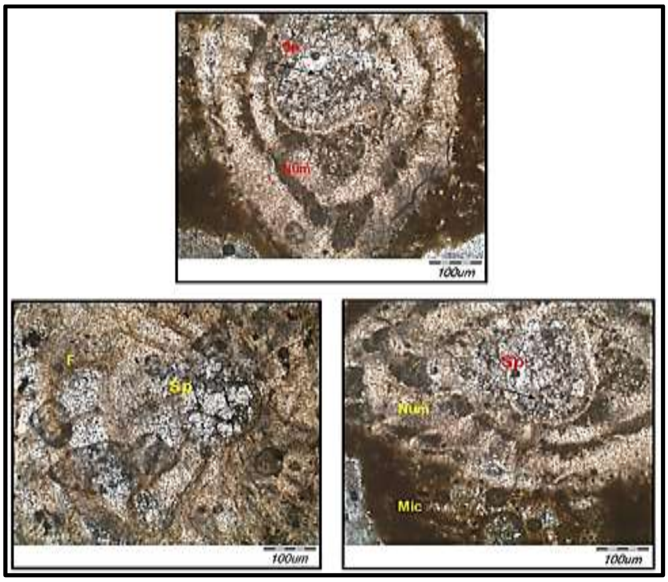

Fig. 8. Photomicrographs of the studied limestone.

Mineralogical analysis by XRD

The analysis by XRD indicated that the stone sample taken from the funerary stela consists mainly of calcite (CaCO3) as shown in fig. (9), and this was matched with XRD analysis of the experimental study stone (fig. 10), which also agrees with the result of the investigation by polarizing microscope for the experimental study stone as it composed substantially of calcite as the main component.

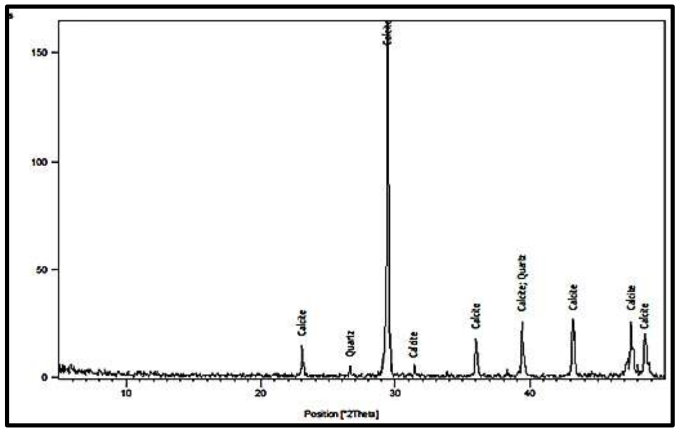

Fig. 9. X-ray diffraction pattern of the monumental stone.

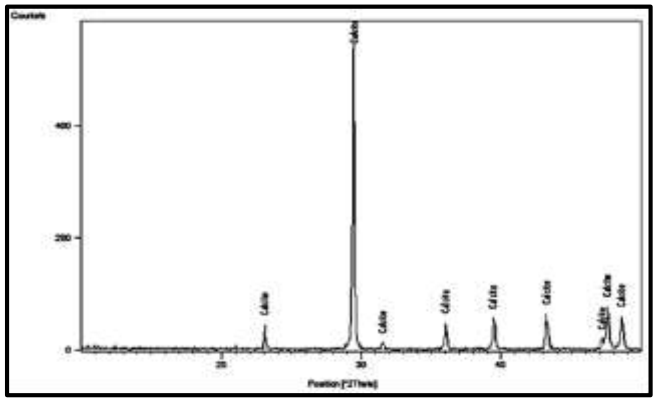

Fig. 10. X-ray diffraction pattern of the experimental study stone.

Appearance changes

After the treated samples have dried completely, by visual observation, no color change is detected in the surfaces of treated samples by DAP compared to the reference sample ((it will be referred in this paper with the acronym "UNTR"). While samples treated by TEOS showed a noticeable yellowing, as shown in Fig. (11).

Fig. 11. Effect of consolidants on the appearance of treated samples compared to the reference sample (UNTR).

Physico-mechanical properties of the studied samples

Three specimens were used in each test, in order to obtain statistically reliable results. The average values of the studied physico-mechanical properties of references and treated samples are listed in table (1) and represented graphically in fig. (12). The obtained results proved that there are clear differences in the samples physico-mechanical properties due to the consolidation efficacy of the materials used. The obtained measured physico-mechanical average values revealed that treated samples by DAP achieved more efficiency than TEOS treated samples. As treated samples by DAP have average values of bulk density and uniaxial compressive strength exhibited clearly increase and improvement than others treated by TEOS.

Table (1). The change in physico-mechanical properties of the treated samples compared to the Ref. sample (UNTR).

Samples \ Properties		Bulk density (g/cm^3)	Water absorption (%)	Apparent porosity (%)	Uniaxial compressive strength (Kg/cm^2)
Standard sample		1.9	11.65	24.2	83
Treated samples	by DAP	2.2	10.2	22.4	137
	by TEOS	2.1	9.0	19.36	103

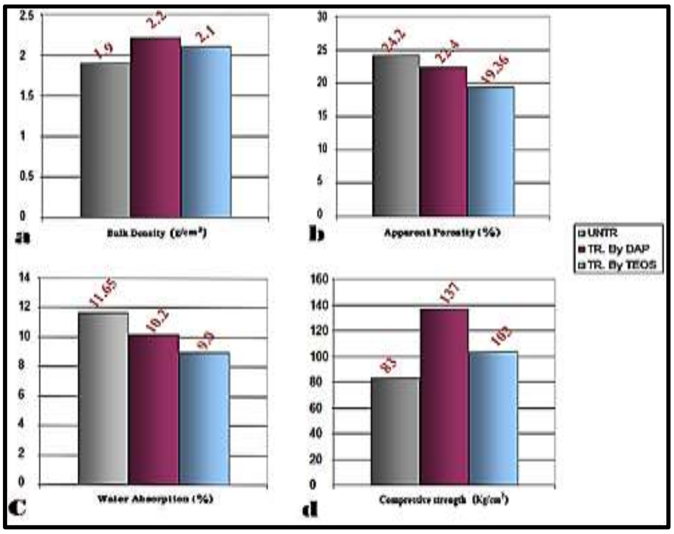

Fig. 12. Physico-mechanical measurements of the Ref. and treated samples: (a) bulk density, (b) apparent porosity, (c) water absorption, and (d) compressive strength.

SEM investigations of fresh, treated and weathered samples

Scanning electronic microscopic investigation (SEM) for the treated samples, showed different forms of consolidants penetration in the samples. SEM results of treated samples proved that the morphological features of these samples were highly affected and changed after treatment as shown in fig.(13):

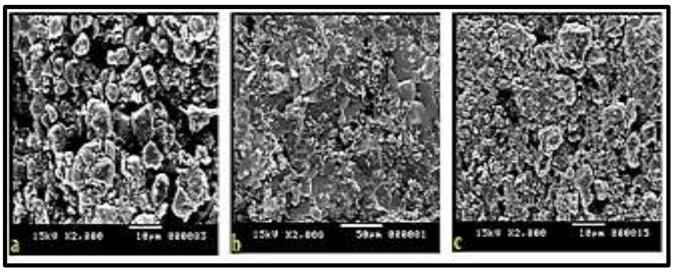

Fig. 13. SEM photomicrograph shows: (a) SEM photomicrograph of the untreated sample shows a wide field of the grains consisting stone; (b) treated sample by DAP and shows a mostly filling by a considerable amount of hydroxyapatite; (c) SEM photomicrograph of the sample treated by TEOS shows a partially formed calcium silicate phase between the pores.

It is noticed from the previous SEM photomicrographs of the treated samples by diammonium hydrogen phosphate (DAP) and TEOS compared to the standard sample (UNTR), that the morphological features of these samples were highly affected and changed after treatment as there is a good diffusion of the two consolidants inside the stone pores, but the superiority of DAP over TEOS is also evident. This was reflected on the physico-mechanical properties of the treated samples.

5-Discussion

The basic principle of stone consolidation is to introduce a compound that penetrates into the stone and reestablish grain to grain cohesion either by forming a bridge between grains or by forming a continuous film. However, the consolidated stone must not be stronger than the unconsolidated one or the strengthened zone at the surface. Also, it must be compatible with the unconsolidated stone in terms of color, water absorption, water vapor transmission, and thermal expansion [26]. Inorganic-mineral consolidating products are based on the penetration of water-soluble chemical precursors that _following mechanisms of hydrolysis, carbonation, or chemical interaction with the stone substrate_ develop a crystal-texture of neo-formed insoluble products that causes the consolidating effect [32]. The experimental results presented above show that the studied samples behavior before and after treatment are completely changed. It is certain that there were important changes in the stone properties due to the use of different consolidant types [33]. In order to analyze the efficiency of these consolidants and to define these changes, some of these properties were laboratory evaluated as follow:

Textural investigations and mineralogical analysis

Results of the polarizing microscope proved that the studied stone is fossiliferous limestone [34,35]. This type of limestone is made mostly of calcium carbonate (CaCO3) in the form of the calcite or aragonite minerals, which contains an abundance of fossils or fossil traces [36]. XRD analysis of the sample taken from the funerary stela confirms that the stone is substantially composed of calcite as the main component and agreed with XRD analysis of the experimental samples.

Visual observation

Color change one of the most important characteristics that strongly contribute to the ornamental value of building materials [37]. It was used to determine the color differences caused by consolidation treatments [38]. According to [39], color photography, the technique most frequently used in conservation, is an effective tool for quickly documenting the color and condition of objects. The results in Fig. (11) show that there is a noticeable yellowing in the treated samples by TEOS, which will distort the monument, and this is considered completely unacceptable.

Physio-mechanical properties changes caused by consolidation processes, Fig. (12) were evaluated through comparing the measurements of the major physio-mechanical properties of the samples before and after treatment. Generally, it could be claimed that all density "B" measurements changed in the treated samples compared to the un-treated ones (Table 1). Where the density value of the samples treated by DAP recorded 2.2 (g/cm3), and the samples treated by TEOS recorded 2.1 (g/cm3), compared to the reference samples recorded 1.9 (g/cm3). These increases were connected to the consolidation effects and they were mostly owed to the good penetration of the consolidants within the stone pores which was confirmed by other researchers in similar cases [40-42].

In addition, the decreasing of apparent porosity "AP" index after treatment processes, where, it records (22.4%) in samples treated by DAP and (19.36%) in samples treated by TEOS. The decreasing of this index after consolidation revealed the succession of the 2 types of consolidants in achieving their essential aims [43].

Water absorption coefficient "WA", is one of the most important parameters that characterize the capillary water uptake by the stone. From the obtained results, it could be said that there are noticeable variations between the water uptake behavior against the consolidant materials through their ability to reduce this index in the samples. Correspondingly with the negligible reduction of stone porosity, water uptake of the samples after Phosphate-treatment changed slightly, where it recorded 10.2% compared to the untreated reference samples which recorded 11.65%. While TEOS treatment dramatically alters water transport properties of the samples, even after 4 weeks of curing. Obtained results of TEOS-treated samples exhibited negligible water uptake for 24 hours of contact with water, where it recorded 9.0%. This can be ascribed to the reduction in samples porosity and, mostly, to the temporary hydrophobic effect of ethoxy groups, that remain in the stone until curing reactions are complete [44,45]. This may require several months [46,47], during which it is impossible to apply any water-based treatment [44,45]. Moreover, according to [44] in case of water can enter the stone from behind the TEOS-consolidated stone layer (e.g., because of rising damp, not completely eliminated before the consolidation intervention, or because of condensation or infiltration), problems may arise during the period of temporary hydrophobicity, as water is blocked behind the consolidated layer and damage owing to salts and/or freezing-thawing may occur.

Uniaxial compressive strength "C" is one of the most important parameters used to evaluate the consolidants efficiency by comparing its values before and after treatment [48]. Additionally, it represents an important indicator of compactness and of the possible change of total porosity of material, and of the durability too [49]. Through the data presented in Table (1), it could be noticed that "C" values increased in the treated samples due to the effects of consolidation process according the consolidant type, Where, it records an increasing index (137 Kg/cm2) in the samples treated by DAP and (103 Kg/cm2) in the samples treated by TEOS. It is clear that the treated samples by DAP were much more durable than the treated samples by TEOS, and this agrees with [8], who pointed out that the percent strength increase for limestone after ethyl silicate treatment is not as great as for sandstone.

According to [10], TEOS effectiveness is known to be dependent on the presence of quartzitic fractions inside the substrate, allowing for chemical bonding. The reduced effectiveness of TEOS treatment on carbonate substrates, compared to silicate ones, the temporary hydrophobicity of TEOS-treated stones and TEOS tendency to crack during drying are the main limitations of this consolidant when applied on carbonate stones.

SEM investigations. Superiority of samples treated by DAP as SEM photomicrographs showed mostly filling by a considerable amount of hydroxyapatite, and this was reflected in the mechanical properties of the sample treated by DAP, where it showed a clear improvement in its mechanical properties.

6-Conclusions

The different physico-mechanial and surface hydrophobation can be used as parameter for evaluating the different impact of both used innovative consolidants on studied monumental limestone.

Transport properties of the treated stones by DAP slightly altered so that water and water vapor exchanges between the treated stone and environment are not significantly blocked, this is one of the most promising properties of hydroxyapatite.

The application of a 3 M DAP solution by capillary absorption, followed by application of a limewater poultice, proved to be a very effective method to enhance the studied limestone mechanical properties.

DAP consolidant showed higher efficiency in improving the mechanical properties, much better than TEOS.

Yellowing of the samples treated by TEOS made its use in the current study completely rejected.

Finally, and based on all of the results reported in this paper, DAP would be the most efficient for studied limestone consolidation in the present case, whereas it was found that it totally improved the stone properties, in addition to its high compatibility with the stone substrate.

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