

INFLUENCE OF ACRYLIC COATINGS AND NANOMATERIALS ON THE INTERFACIAL, PHYSICAL, AND MECHANICAL PROPERTIES OF LIMESTONE-BASED MONUMENTS. CASE STUDY OF “AMENEMHAT II TEMPLE”

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Abstract

The present paper covers the study of limestone consolidants based on acrylic polymer (Paraloid B-72), $\text{Ca}(\text{OH})_2$ nanoparticles (Nanolime) and the acrylic polymer mixed with $\text{Ca}(\text{OH})_2$ nanoparticles. The experimental study was conducted on limestone samples from El-Ashmunein archaeological area, Minia, Egypt. Some tests were done for studying the behavior of the consolidants used. The main goal of these tests was to estimate the consolidants efficiency and investigate the changes of physio-mechanical properties of the studied samples before and after consolidation, as well as after artificial aging. Therefore, laboratory measurements such as weight change, chromatic variations, physio-mechanical and SEM were performed. It was observed that there are noticeable differences among stone physio-mechanical properties of samples after treatment and after artificial aging according to the types of consolidant. It was found out, the best efficiency was the mixture of Paraloid B-72 and $\text{Ca}(\text{OH})_2$ nanoparticles, followed by $\text{Ca}(\text{OH})_2$ nanoparticles (Nanolime) dispersion in ethanol 2.5%, then Paraloid B-72 2%. The obtained results showed a significant improvement in physio-mechanical properties of the samples treated by the mixture of Paraloid B-72 and $\text{Ca}(\text{OH})_2$ nanoparticles, e.g., increase in bulk density from 2.02 to 3.55 g/cm^3 and decrease in porosity from 25.09% to 13.74%, as well as a noticeable increase in compressive strength.

Keywords: Nanoparticles; Consolidants; Powdering; Efflorescence; Compressive strength.

Introduction

Conservation is one of the most complex topics in the materials science as it requires interdisciplinary expertise ranging from the architecture, the technology of materials to the advanced analytical and physical chemistry [1]. Consolidation represents a very difficult and delicate operation in the conservation and restoration field, as it might cause undesirable effects, such as yellowing, formation of aggressive substances and heterogeneous distribution into the support [2-4]. Consolidation material is required to have two main properties adhesion and cohesion to finally provide the object with mechanical strength and physical properties [5]. Stone consolidants are applied as liquids but, to be effective, they must cause a solid material to be laid down in the pores of the stone that will act as cement and restore the intergranular bonds [6]. Recent developments have shown that the complex tasks of the conservation of the cultural heritage can be solved very effectively using novel nanomaterials and nanotechnology methods. Nanotechnology is a new technological revolution, one so profound that will touch all the

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aspects of human society [1]. Nanotechnology is an emerging field of science related to the understanding and control of matter at the nanoscale, i.e., at dimensions between approximately 1 and 100 nm (this dimensions are known as the Nano-scale) [7-9]. The innovative properties of nanomaterials can have advantageous application in the restoration and conservation of the cultural heritage with relation to the tailoring of new products for protection and consolidation of stone [10]. The essence of nanotechnology is the ability to control matter at the nanoscale, that is at the level of atoms, molecules, and supra molecular structures to generate structures with fundamentally new molecular organization [11]. The term nanotechnology comes from the combination of two words: the Greek numerical prefix "Nano" referring to a billionth (1×10^{-9}) [12-15] and signifying "dwarf" [16], is becoming increasingly common in scientific literature, and the word "technology" [17]. The present paper is an experimental study for limestone consolidation using a traditional and nanomaterial consolidants. It included a study of deterioration factors affecting Amenemhat II temple in El-Ashmunein archaeological area, Minia, Egypt and the deterioration forms of the temple. This temple was built of limestone blocks and dates back to the Middle Kingdom. Only a few parts of the temple remained, it having in all probability (Fig. 1), served as a convenient quarry for the activities of later builders [18].



Fig. 1. Amenemhat II temple at El-Ashmunein archaeological area

This temple has suffered from many deterioration factors over the years, resulting in the loss of a lot of parts, as the figures show later; only a few parts survived. The deterioration factors affecting the temple include temperatures and relative humidity average, wind action, air pollution, biological factors and the rise of groundwater level, which is considered the most serious deterioration factors affecting the temple, (Fig. 2).



Fig. 2. Some of the deterioration factors affecting "Amenemhat II temple"

The study of the deterioration forms in "Amenemhat II temple" in El-Ashmunein (Fig. 3) has shown a wide range of deterioration forms including powdering, scaling, flaking, black crust, efflorescence, cracking, blistering and chipping [19].

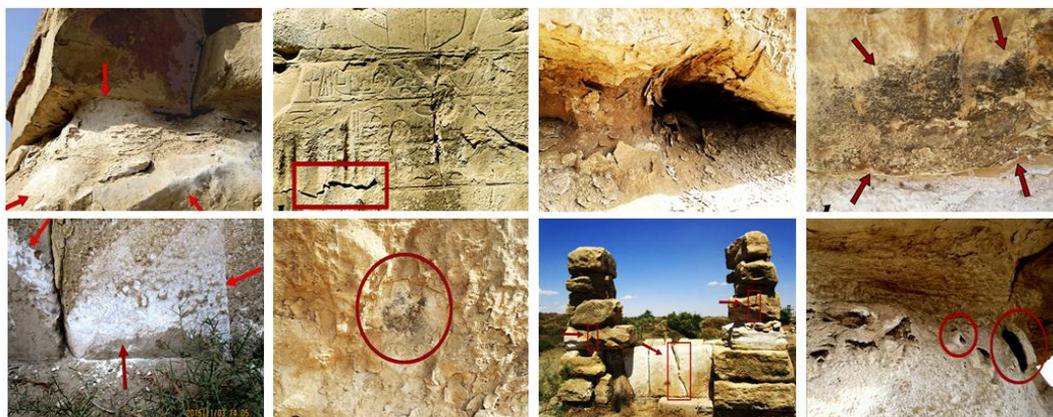


Fig. 3. Some deterioration forms present in "Amenemhat II temple": powdering; scaling; flaking; black crust; efflorescence; sub-efflorescence; cracking and blistering

Experimental

Characteristics of the materials used

According to some previous studies [20, 21] some thin sections were prepared for petrographic investigations using polarizing microscope (Olympus BX50, Japan) associated with computer software imaging system called (analysis). Furthermore, an XRD analysis was conducted to identify the mineralogical compositions of the samples using JEOL X-ray diffractometer model JSX-60 PA of the Central Laboratory, Minia Univ. The analysis was conducted with Cu Ka radiation, Ni filtered ($\lambda = 1.54184\text{\AA}$) at 35kV and 15mA, under a normal scanning speed of 2/1 minute, within the range of $2\theta = 4-100^\circ$. These investigations aim to identify the mineralogical composition, texture, fabric and micro-structure of the samples before treatment. Additionally, it aims to identify the presence or absence of weathered or altered minerals and their effect on the properties of the stone. Scanning electron microscope, JEOL JSM-5400LV, was used to determine the morphological and microstructural characterization of the particles and voids. In addition to detect the consolidants penetration efficiency for the treated samples and detect the effect of salts crystallization tests after artificial aging. Finally some physical properties were defined before treatment to evaluate the differences due to the consolidation efficacy of the materials used.

Treatment processes

The experimental study was carried out on some samples of neglected limestone blocks collected from El-Ashmunein archaeological area. The samples were prepared on cubes ($5\times 5\times 5\text{cm}$) and they were used as a target for the consolidation process using acrylic polymer (*Paraloid B-72 2 % in acetone*), $\text{Ca}(\text{OH})_2$ nanoparticles (*Nanolime 2.5% in ethanol*). They were divided into three groups (*A*) treated by Paraloid B-72, (*B*) treated by Nanolime and (*C*) treated by Nanolime in iso-propanol with Paraloid B-72. According to literatures [7, 22-24], 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. 4).

This process is necessary to have knowledge of the efficiency and future evaluation of the products against the samples durability. Finally, the treated stone was removed and was dried at room temperature for 60 days until the complete polymerization.

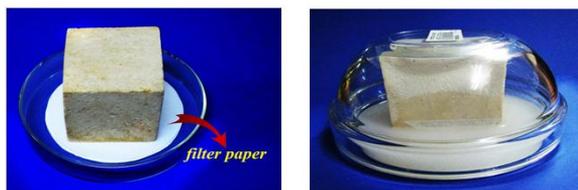


Fig. 4. Prepare the samples and place them in the consolidant with careful covering process

Aging processes

The evaluation of consolidation efficiency in terms of improving the resistance of treated samples to the deterioration phenomena caused by weathering effects takes place through dynamic artificial accelerated tests. So, the aging processes are important for studying the samples characteristics after a long time of chemical treatment and consolidants application. Hence, it is necessary to design a plan of accelerated aging in laboratories in order to study and evaluate the relation between stonework and these materials and to define the most suitable ones for site application [22, 25]. The present study involves the following ageing tests: 1) Salt crystallization test and 2) Heating and cooling cycles (thermal shock).

Salt crystallization test

The test is determined 15 cycles according to (BS EN 12370-1999) which involves the following: before the test, the samples must be cleaned and dried till constant weight at 60°C and recording their original weight (M_0). Each cycle consists of 2:4 hours of total immersion in a 14% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ solution and 18 hours of drying in the oven on 60°C (instead of 105°C). After the drying phase, the samples were left to cool down to room temperature during 2 hours by the end of which their weight was recorded. The samples durability test against salt crystallization (salt crystallization test) can be calculated according to the following equation:

$$\Delta M = 100(M_n - M_0)/M_0,$$

where: ΔM - the sample durability, M_0 - the original dry mass in grams and M_n - dry mass of sample in grams after 15 cycles.

Thermal shock (heating-cooling cycles)

Thermal shock refers to the stress that a stone tile undergoes when it is subjected to an abrupt temperature changes, inside as well as outside. The test was carried out according to (BS EN 14066-2003). Within the same context, after drying to a constant mass, the samples underwent 30 cycles of drying at $105 \pm 5^\circ\text{C}$ followed by immersion in water at $20 \pm 5^\circ\text{C}$. After this test the physico-mechanical properties were measured again. The loss in weight was measured in the same manner such as in salt crystallization test [19]. After finishing these processes, depth of penetration, chromatic variations, weight changes and measuring the contact angle (θ) were conducted. In addition these evaluating procedures were reused for evaluating the state of tested samples after finishing both treatment and aging processes.

Results

Polarizing microscope investigations of fresh samples

Results obtained show that all the studied samples by thin section photomicrographs techniques showed that they consist essentially of fossiliferous limestone (Fig. 5). Most abundant fossiliferous are *Nummlites* and different types of *Foraminifera*.

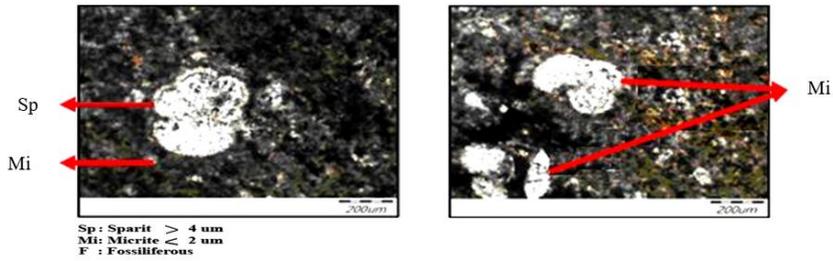


Fig. 5. Photomicrographs of the studied limestone

X-ray diffraction (XRD) of fresh samples

The analysis indicated that the temple stone (sample 1 and 2) and the stone from which the experimental samples were cut (sample 3) have the same mineralogical composition, where they essentially consist of *Calcite* (CaCO_3) in addition to *Halite* (NaCl) as a trace. In addition, the analysis of the other samples showed the presence of different salts such as *Thenardite* Na_2SO_4 , *Halite* (NaCl), *Aphthitalite* $[\text{K}_3\text{Na}(\text{SO}_4)_2]$, *Trona* $[\text{Na}_3\text{H}(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ and *Sylvite* (KCl), as shown in Figure 6.

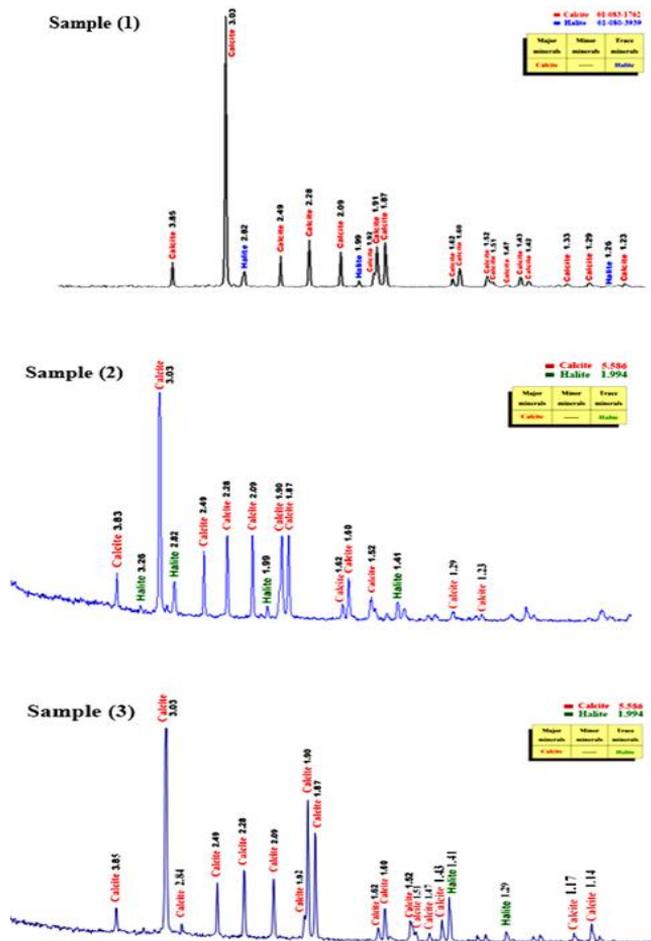


Fig. 6. X-ray diffraction patterns of the investigated samples

Depth of penetration, chromatic variations and weight change of fresh, treated and weathered samples

Through laboratory observations it could be claimed that there are big differences in the time of penetration between the treated samples according to the consolidant types as shown in Figure 7. In addition, it could be noticed that there aren't any chromatic variations detected in the samples surfaces both after treatment and after artificial aging in the samples, as shown in Figure 8. Within the same context, the measurements of treated samples net weight after artificial aging were changed according to the consolidant type as listed in Table 1.

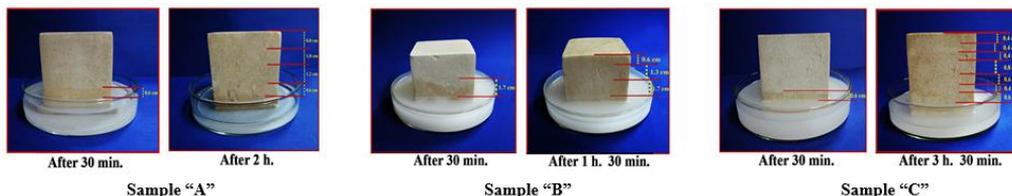


Fig. 7. The time of consolidants penetration in some experimental samples



Fig. 8. Effect of consolidants on the appearance of treated samples compared to the reference sample (A)

Table 1. Average weight loss ΔW% of all studied samples after accelerated aging processes

Samples	R	A	B	C
Avg. ΔW%	6.03	4.38	3.75	2.08

Measuring the contact angle (θ) of fresh, treated and weathered samples

Regarding the micro drop test, it could be argued that there are some variations in static contact angle measurements, which give an indication of hydrophobation differences according to the applied consolidant. In addition, the obtained results revealed that the contact angle of the surface increased with the addition of the nanoparticles, as listed in Table 2 and shown in Figure 9.

Table 2. Showing the results of measuring the contact angle (θ) of the studied samples

Sample	left	right	Mean [contact angle (θ)]	height	width
R	19.2	32.9	26	0.481	7.388
A	9.5	180	94.8	0.198	6.524
B	50.4	180	115.2	0.332	7.848
C	19.5	180	99.8	0.419	5.574

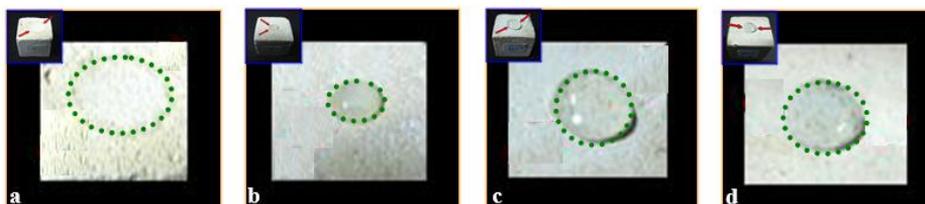


Fig. 9. Micro-drop test: water droplet on the studied samples surface

Physico-mechanical properties of fresh, treated and weathered samples

Although all samples were cut off from the same block (except the reference sample A), the measurements of physico-mechanical properties of treated samples proved that there are big differences in the samples physico-mechanical properties due to the consolidation efficacy of the materials used. The results of physico-mechanical properties of the reference, treated and weathered stone samples by salt crystallization test are listed in Table 3.

Table 3. Change in physico-mechanical properties of the treated and aged samples compared to the reference sample

Properties	Investigated Samples							
	R (Ref S)		A		B		C	
	Un T.	A. Age	A Tre.	A. Age	A Tre.	A. Age	A Tre.	A. Age
Bulk density (g/cm ³)	2.02	01.87	02.40	02.36	02.51	02.46	03.55	03.49
Apparent porosity %	25.09	27.13	18.68	19.04	16.61	16.97	13.74	13.98
Water absorption %	11.26	12.18	09.46	09.64	09.08	09.28	06.41	06.52
Compressive strength (Kg/cm ²)	106.0	66.67	119.59	100.64	158.46	129.86	176.9	156.4

Un T. = Un treated samples, A Tre. = Treated samples, A Age = Aged samples

SEM investigations of fresh, treated and weathered samples

Scanning Electronic Microscopic (SEM) investigation of the treated samples showed different forms of consolidants penetrated in the samples. Also, they proved that the morphological features of these samples were highly affected and changed after treatment, (Fig. 10-a, b and c), where, the SEM photomicrograph of untreated sample A (the reference) showed distribution of calcite grains consisting the sample. Moreover, some inter-crystalline pores were clearly observed, while the SEM photomicrograph of sample B (the sample treated by Paraloid B-72 2%) showed the presence of consolidant between treated stone grains (forming agglomerated grains, known as adhesion process).

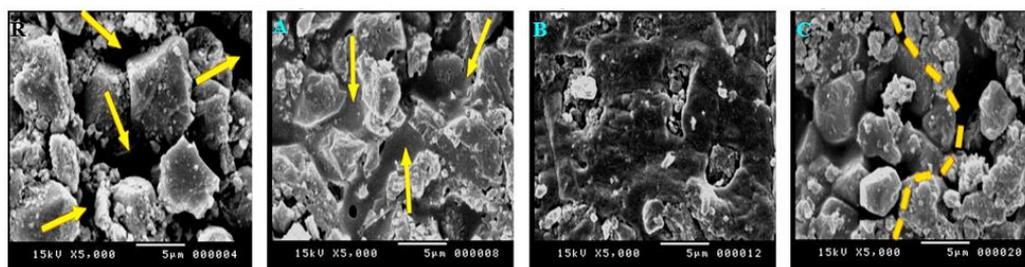


Fig. 10. SEM image showing the morphological features of the reference sample (A) and the treated samples (B, C and D)

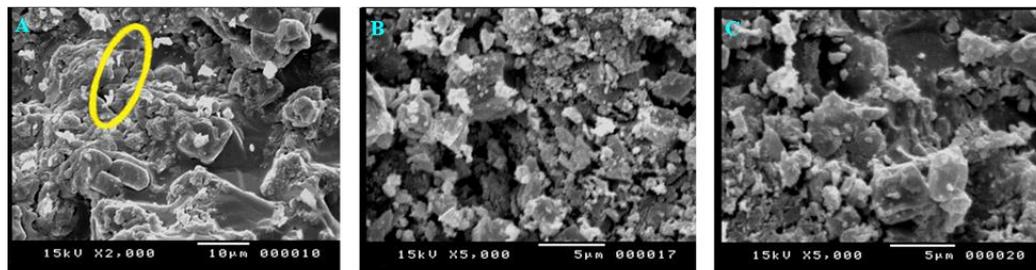


Fig. 11. SEM image showing the morphological features of treated weathered stone samples (B, C and D).

SEM photomicrograph of sample C (the sample treated by *Nanolime* dispersion in ethanol 2.5%) showed formation of sub mature CaCO_3 crystals formed deeply in pores and between grains (known as pore filling process). SEM photomicrograph of sample C (the sample treated by $\text{Ca}(\text{OH})_2$ nanoparticles dispersion in iso-propanol with *Paraloid B-72*) showed a duplicate consolidation forces process occurred by partially pores filling using *Nanolime* (the right side in the image) and also, adhesion by *Paraloid B-72* (the left side in the image). On the other hand, SEM observations of aged samples showed the presence of *Thenardite* Na_2SO_4 , in addition to the presence of a crack affected the samples treated with *Paraloid B-72* (Sample B), (Fig. 11).

Discussion

The recent development of nanoscience and nanotechnology has opened the way to new applications in many scientific fields, including the conservation of cultural heritage such as “Nanolime” [26]. In this regard, there are several factors influencing the effectiveness of these materials as consolidants such as: materials characteristics, solvent type and concentration, particle size, morphology etc, in addition to physio-mechanical properties of the substrate itself [27]. Different physio-mechanical properties and chemical characteristics of building materials may be changed due to the effects of consolidation processes [22, 28-30]. In order to analyze the efficiency of these consolidants and to define these changes, some of these properties were laboratory evaluated in two states. In each test, three samples were evaluated before treatment (R group) and after treatment and aging substantially process (A, B & C groups) as follow:

Evaluation of stone substrate before treatment

Results of the *polarizing microscope* proved that the fresh samples consist of fossiliferous limestone [31, 32]. This type of limestone is made mostly of calcium carbonate (CaCO_3) in the form of the minerals calcite or aragonite, that contains an abundance of fossils or fossil traces [33]. *XRD analysis* confirms that the building stones of Amenemhat II temple substantially composed of calcite as a main component which was obviously affected by the high level of saline groundwater; direct reason for the existence of most of the deterioration products [34]. Within the same context, the occurrence of *Halite* [NaCl] is fundamentally due to the application of large amounts of irrigation water to soils, the presence of salt-bearing sediments and formation of evaporation underlying the surrounded agricultural area as attested previously by *Scanlon et al.* [35]. In addition, the presence of *Aphthitalite* [$\text{K}_3\text{Na}(\text{SO}_4)_2$] appears as a sub-efflorescence which has grown in parallel bands within the porous material [36]. It occurs as colorless or yellowish-orange groups of inter-penetrating bladed, tabular crystals or fine-grained aggregates [37]. In the present case study, it could be formed as a salty accumulation due to the interaction of solutions formed from pigeon droppings with porous limestone causing a notable deterioration in limestone due to acid attack as demonstrated in a similar case [38]. *Trona* [$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$] appears as the principal deterioration product of our stone body, it was formed after the reaction of atmospheric carbon dioxide with sodium ions [39]. In addition, it may exist due to the dominating environmental effects such as precipitating of carbonate salt from seepage waters evaporation [40] or due to the zoned evolution of sodium salts by interaction between solutions from a deposit of common salt and the wall mortars [41]. Finally, the presence of *Sylvite* (KCl) in a cubic shape is owed to its high solubility as attested previously by *Ganor et al* [42]. It mostly occurred due to chemical reaction and ion exchange between Ca as a source of *Calcite* and potassium nitrate present in salinity water. This salt is extremely dangerous because it has a high ability to re-crystallize in humid environments causing several form of deterioration [43].

Evaluation of stone substrate after treatment and aging processes

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 [22]. So, the consolidant materials are usually tested after consolidation and aging processes for evaluating their influences on the treatment process. The experimental results presented above show that the studied samples' behavior before and after treatment, and artificial aging are completely changed. It is certain that there were important changes in the stone properties due to the use of different consolidant types [44].

Depth of penetration, (Figure 7), it could be claimed that the time of penetration was (1½ h.) in the samples treated by *Nanolime* dispersion in ethanol 2.5%, the samples treated by *Paraloid B-72* 2% (2 h.), and (3½ h.) in the samples treated by *Nanolime* dispersion in isopropanol with *Paraloid B-72*, respectively. This may be due to materials' viscosity, surface tension and rate of deposition [45], as well as the effects of solvent types, their evaporation rate and liquid transport within the pores. It was found that solvents with high boiling points improved the depth of material deposition in stones with large pores (35-40µm), while solvents with lower boiling points performed better in materials with finer pores (0.5-2µm which reduced *Nanolime* migration back to the surface during the solvent drying) [46]. Additionally, some structural variations of the stone itself such as the pore structure (*microstructure porosity, pore shape and pore connectivity*), in addition to properties of consolidation products [47].

Chromatic variation or color change one of the most important characteristics that strongly contribute to the ornamental value of building materials [48]. It was used to determine the color differences caused by consolidation treatments [49]. The findings in Figure 8 illustrate that there were undetectable chromatic variations which affected both the treated samples and aged ones. This maybe due to the stability of main mineral colors (*Calcite as a unique mineral*) or internal rock structure and its surface texture [50]. On the other hand, these undetectable variations after artificial ageing were attributed essentially to the un development of different features of patina contrary to the findings presented by *Vicente & Brufau, 1986* [51]. Table 1 show that there are notable *weight change* rates between the reference samples (R) and treated aged ones. The recorded decreasing rates are as follow: sample (A 4.38%), (B aprox. 3.75%) and (C aprox. 2.08%). According to *B.Miglio, et al.* [52], the studied samples (A, B and C) belong to class B durability (*characterizes by decreasing rate due to crystallization loss 1:5 %*), while, the reference samples R belong to class C of durability (*characterizes by decreasing rate due to crystallization loss > 5:15%*). From a specialized point of view, it could be claimed that these variation maybe attributed to the different behaviors of salt crystallization process, evaporation rates [53-55] with different types of consolidants and solutions. Additionally, they may be due to the leaching processes that affected the stone bodies during salt crystallization test [56].

Contact angle was determined by the resultant force of the cohesive liquid-liquid molecular forces and the adhesive solid-liquid forces depended on the characteristics of the solid and liquid involved [57]. This test is visually conducted through defining consolidant transference in the samples by measuring the angle between the microdrop and substrate surface which indicated the water repellency index. The obtained results, Figure 9, revealed that the contact angle of the treated aged samples increased compared to the reference one. Furthermore, the same angle increased with the increasing nanoparticles percentage in the samples, as follows. The recorded highest value of contact angle was to the (*samples of groups B = 115.2*), followed by (*samples of groups C = 99.8*) and (*samples of groups A = 94.8*). Consequently, the *Nanolime* in ethanol 2.5% - based treatment strongly altered the rate of water sorption and hence the total water absorption as a consequence of both the modifications in pore size distribution as attested by *Sassoni et al.* [58] in similar case. In fact, these variations were essentially attributed to the hydrophobicity according to the applied consolidants. They had

surfaces a static contact angle ($\theta > 90^\circ$), in addition to the water beads-up on the surface and tried to minimize contact with surface (water-fearing surface) [59, 60].

Physio-mechanical properties changes caused by consolidation processes, Figure 12 were evaluated through comparing the measurements of the major physio-mechanical properties of the samples before, after treatment and accelerated aging [22, 61]. Through evaluating the data, these changes were mostly attributed to the distinctive optical, electronic, electrical, magnetic, chemical, and mechanical properties of the applied nanomaterials [1]. Generally, it could be claimed that all *density* " γ_d " measurements changed in the treated samples compared to the un-treated ones even after aging processes (Table 3).

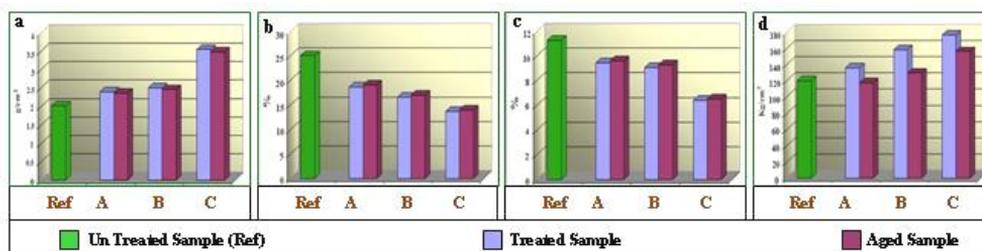


Fig. 12. Physico-mechanical measurements of un treated samples (Ref), treated and aged samples: a. density, c. porosity, b. water absorption and d. compressive strength.

They record an increasing rate (26.2%) in group (A), (31.5%) in group (B) and (86.6%) in group (C). 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 [62-64]. In addition, the decreasing of *Porosity* " η " index both after treatment processes and accelerated aging cycles recorded (-29.8%) in group (A), (-37.4%) in group (B) and (-48.5%) in group (C). The decreasing of this index after consolidation revealed the succession of the 3 types of consolidants in achieving their essential aims (*releasing of moisture and unsealing the stone surfaces*) [65]. By comparing the results in table (3) it could be claimed that the consolidant applied to group (C) caused a significant change in porosity and reduced its value more than other two types which led to achieve good hydrophobic properties of treated stones. These good hydrophobic properties resulted essentially from decreasing the pores size, enhancing the surfactant elimination and creating a dual roughness scale (micro and nano), as argued by *Zornoza-Indart, et al.* [66]. In addition, this type was responsible for substantial alterations in the pore size distribution, even if the open porosity was not completely occluded [67] which finally improved resistance and hydrophobic characteristics, as well as increasing its flexibility. Thus, prevented the cracking [68] and other deterioration forms. *Water absorption coefficient* " WA ", is one of the most important parameters that characterize the capillary water uptake by the stone. From the extracted data in table (3), 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. It decreased in all investigated samples as follows: (-22.33%) in group (A), (-23.81%) in group (B) and (-46.46%) in group (C), which was owed to the reliable effectiveness of these materials as attested by *Pinho & Mosquera* [69] in a similar case. This effectiveness was closely related to the pore structure, the pore radius and the porosity, the behavior of the materials, pore size and distribution which allow access to treatment within the rock through defined mechanism [55, 56]. This mechanism that increased the ability of preventing the water penetration through the pore system [70] created a greater resistance to capillarity water absorption, then good water repellent properties. Regarding the great reducing of capillarity water absorption coefficient with group (C), it could be claimed that it was related to the chemical combination between nanostructured product (*Nanolime*) with normal product

(Paraloid B-72) [68] that created a complex network within the stone pores. *Uniaxial compressive strength* “ σ_c ” is one of the most important parameter used to evaluate the consolidants efficiency by comparing its values before and after treatment and artificial ageing [71]. Additionally, it represents an important indicator of compactness and of the possible change of total porosity of material, and of the durability too [72]. Through the data presented in Table 3, it could be noticed that “ σ_c ” values increased in all samples due to the effects of consolidation process according the consolidant type, Where, it record an increasing index (51%) in group (A), (94.8%) in group (B) and (134.65%) in group (C). These increases essentially resulted from the strengthening and stabilizing of all friable weathered surfaces, which agreed with the concept of that increasing porosity decreases strengths and vice versa [73]. Several works concerning the influence of water content on the engineering studies done by some researchers [74-78] showed that the compressive strength of rocks was reduced by saturation with water. In addition, it resulted from the function of the grain size which was re-distribution and re-composition due to consolidant interferences with the pores [79]. This ensured Griffith's theory which showed that the compressive strength should rise dramatically when confining pressure [80] due to filling the stone pores by consolidants.

SEM investigations, (Figure 10) showed, on one hand, the untreated sample (R) that stressed calcite grains which were highly affected by dominated deterioration factors [81], some inter-crystalline pores and disintegrated grains were clearly observed. On the other hand, significant differences in stone samples (A, B and C) were observed after the treatment processes, including no signs of cracks. These differences reflect the presences of consolidant features within the stone pores adhering its grains [82]. Sample treated by *Paraloid B-72*, figure (10-a) showed insignificant change in the consolidant distribution possibly due to its low penetration depth, (about 2-4mm) as reported by *Perez, et al.* [83] in a similar case. Moreover, it could be deducted that all nanomaterials treatments not only coated the pores, but it also spread out and impregnated through the whole treated samples. This is essentially attributed to the characteristics of nanomaterials that had sub micrometric sizes (Figure 10b and c) characterized by a rounded to hexagonal plate-like shape morphology [46]. Nanoparticles tended to aggregate into micron-sized clusters, displaying very irregular shapes; the presence of those clusters of plate-like nanoparticles could be explained by agglomeration processes [84]. The aged samples, figure (1a, b and c) showed some minor effects on surface layers of consolidants due to the effects of salt efflorescence's [85, 86]. In addition, the salt efflorescence's form of thenardite specie (Na_2SO_4) could be formed due to the dissolving \leftrightarrow recrystallizing processes between anhydrous *Thenardite* and decahydrous *Mirabilite* [87]. Within the same context, the presence of a crack affected the samples treated with *Paraloid B-72* (Figure 11b) maybe attributed to less penetration to the depth area of stone structure and fine stone cracks, in addition to the forming the polymer coating by irregular aggregation of particles as attested by *Aldoasri, et al* [88]. Finally, our consolidants could be rated between (*) - (***) according to their enhancement of different characteristics of treated stone, particularly its different main physico-mechanical properties as listed in table (4).

Table 4. Rating of consolidants according to their enhancement of different characteristics of treated stone

Investigated prosperities	Consolidant types			Notes
	A	B	C	
Depth of penetration	**	***	*	Should be high for avoiding rapid evaporation of the solvents
Chromatic variation	***	***	***	Should be absent for avoiding color changes of the samples
Weight change	*	**	***	Should be moderate for avoiding the environmental effects
Contact angle	*	***	**	Should be high for realizing water repellency index of the samples
Physical Properties	■ “ γ_d ”	*	***	Shows good penetration of consolidation of the stone pores
	■ “ η ”	*	**	Shows releasing moisture and unsealing of the stone surfaces
	■ “WA”	*	**	Shows preventing water penetration and creating water repellency
	■ “ σ_c ”	*	**	Shows strengthening and stabilizing of all friable weathered surfaces
SEM observation	*	***	***	Shows consolidants interferences between and adhering its grains
Total Points	13	22	24	Final Rating is C (Excellent), B (Very good) and A (Good)

A = Paraloid B-72, B = Nanolime, C = Nanolime + Paraloid B-72
 (*) = good, (**) = Very good, (***) = Excellent

Conclusion

The deterioration of the historical buildings is a serious problem that attracts the attention of the researchers all over the world. Therefore, the decay of building stones is often compared to the effects of an illness most commonly a cancer-undermining the status of the building and eventually causing its demise. In the last decades, traditional polymeric organic materials, as consolidants and surface coatings, were used for the conservation of stones and architectural monuments, sculptures, wall paintings etc. In order to avoid all limitations and drawbacks of these traditional consolidants, a new technology for the superficial consolidation of carbonatic rocks based on the application of alcohol dispersions (usually 2-propanol) of $\text{Ca}(\text{OH})_2$ nanoparticles (*Nanolime*) was applied. In the present study, the three types of consolidants, namely (*Paraloid B-72 2% in Acetone*), $\text{Ca}(\text{OH})_2$ nanoparticles (*Nanolime 2.5% in Ethanol*) were applied. The experiments showed that the consolidant (i.e. a mixture of $\text{Ca}(\text{OH})_2$ nanoparticles (*Nanolime*) dispersion in iso-propanol with *Paraloid B-72*) would be the most suitable for limestone consolidation in the present case. However, it was found out that it totally improved the stone properties. Additionally, it was the most durable one against artificial aging processes, followed by $\text{Ca}(\text{OH})_2$ nanoparticles dispersion in *Ethanol 2.5%* and *Paraloid B-72 2%*. Thus, the selection of the most efficient consolidants took into consideration the least chromatic variation, the lowest decrease in water repellent, the highest consolidant penetration depth, and a moderate increase of the mechanical resistance. Furthermore, it is essential to explore the long-term effects and efficacy of consolidants taking into account different environmental conditions before recommending this procedure as a standard method for stone treatment.

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