INTERNATIONAL JOURNAL
OF
CONSERVATION SCIENCE

ISSN: 2067-533X Volume 12, Issue 4, October-December 2021: 1231-1248 www.ijcs.ro

CONSOLIDATION OF ARCHAEOLOGICAL LIMESTONE AND IMPROVING ITS CHEMICAL AND PHYSICAL PROPERTIES

Mohamed HASSANE[1,2*], Hussein M. ALI[1], Tarek NAZEL[3]

[1] Faculty of Fine Arts, Department of Conservation, Minia University, Minia, Egypt
[2] St. Petersburg State Institute of Culture, Palace Embankment, St. Petersburg, Russia
[3] Postgraduate Institute of Papyrus, Inscriptions and Conservation, Ain Shams University, Cairo, Egypt

Abstract

Limestone is the basic building material that has been used extensively in building many ancient temples and monumental buildings and which are exposed on a daily basis to many different factors of damage and different environmental conditions that make them subject to a large degree of deterioration and damage such as different weather conditions such as changes in temperature Relative humidity, pollution, sub-surface water, rain, snow, vibrations, biological impact and other factors of damage. Therefore, it is necessary to see many scientific research studies of the important properties of stones, both physical and mechanical properties, and research. The modern chemicals that work to strengthen and improve the properties of the stone in order to help the restorer in diagnosing the case of infection and choosing the best and most appropriate treatment methods.

***Keywords**: Consolidation; Conservation; Physical and mechanical properties; Water absorption; Compressive strength*

Introduction

Archaeological limestone samples were selected for this study: from El-Ashmunein archaeological area, Minia, Egypt., which contains many temples and stone archaeological buildings that suffer from weakness, damage and deterioration, so the main interests in the study are the possibility of characterizing a specific resin through it under the scanning microscope (SEM), and visualization Resin attaches to gravel, penetration and the possibility of correlating this type of data with aging and specific resin performance. Stones were treated with methyl (MTMOS), Paraloid B 72 and Klucel G, and mechanical and physical properties of the stone samples were measured to reveal the best chemicals used to strengthen the stone samples [1].

The limestone used in historical architectural buildings and stone statues is a guide to the civilization and culture of the past, and it is one of the civilizational and cultural heritage of peoples that must be preserved and protected from the factors of deterioration, deterioration, and weathering factors in order to remain stable and lofty for future generations as a cultural and civilizational heritage [2, 3].

Therefore, it was necessary for the whole world and those specialized in protecting cultural heritage, restoration, and maintenance of antiquities to be concerned with the constant search for the most important chemicals used in treating and strengthening stones and

* Corresponding author mohamed.hassaan@mu.edu.eg

improving their physical and chemical properties so that antiquities and culture of the past remain from one generation to the next in the future [4–6].

The process of restoration and maintenance of monuments and archaeological buildings is considered one of the important processes that have been known throughout history and has turned into a science that is studied and concerned by all countries of the world. Of artistic, historical, civilizational, and archaeological value, provided that it does not diminish or alter the nature of the original antiquities, its architectural styles, or its archaeological character, and during the restoration process, the original parts of the antiquity must be preserved in various ways.

Stone is also known as a natural material that is usually found in the form of huge blocks and consists mainly of one metal with small proportions and varying from other minerals such as limestone and sandstone Limestone is defined as sedimentary rock that may be chemically or organically in formation. Limestone consists of calcite (calcium carbonate - $CaCO_3$ and it is called limestone or limestone or calcite and dolomite - $CaMg(CO_3)_2$ and it is called limestone dolomite to increase the percentage of magnesium in it for 15% [7–11].

Therefore, I will discuss in this research the use of some chemicals used in strengthening the stones of the antique buildings to strengthen a group of stone archaeological samples of limestone and the application of the reinforcement materials on them to see how successful and effective these materials are in strengthening. Then after that, a group of important tests, examinations and analyzes are conducted to measure the physical and mechanical properties of the reinforced samples and to know the success of the used reinforcement materials and to choose the best in the strengthening process.

Experimental part

Materials

A group of antique stone pieces were used, all of which were limestone. The antique stone samples were cut into cubes measuring 5cm square (5×5×5), as in figure 1, which shows the cutting of stone samples. The archaeological stone sample cubes were placed in the dishes, which were considered as a prelude to the application of the stiffening processes.

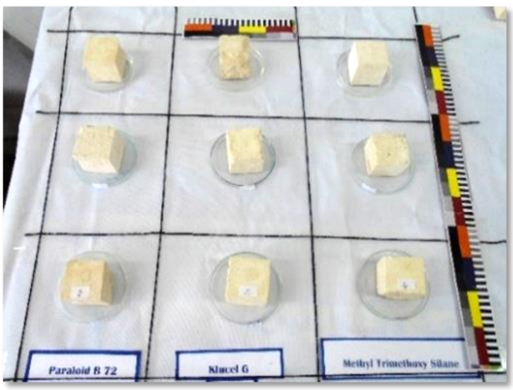


Fig. 1. The preparation of stone samples

Paraloid B 72

It is one of the compounds commonly used to strengthen the effects in general, which is a co-polymer of ethyl methacrylate by 70%, and methyl acrylate by 30%, and it is one of the acrylic products that end up with a group of thermoplastic resins. In the form of transparent colorless crystals, it dissolves in many solvents, the most important of which is acetone and toluene, the most important thing that distinguishes Paraloid B 72 is the high partial weight, and that it does not corrode or dissolve clearly in normal conditions, although oxidation processes and other changes occur to it slowly due to its great penetration into the pores of materials. Construction and network configuration Gel granules are working to link the weak effects of strong parts and is Leakage by capillary action, shows the granules of Paraloid B 72 [11–13].

Klucel G, Klucel, Hydropropylcellulose

It is a white powder or powder colorless and odorless with a code number 63712-63700 and the chemical name is hydroxypropyl cellulose. Cellulose derivatives are characterized by a variety of properties, as they combine solubility in organic solvents, thermoplasticity, activity and diffusion on the reinforced surface. They are characterized by polymer chains of different lengths, so we find that:

- Short chains of polymer Klucel
- Medium chain polymeric Klucel G
- long chains of polymer Klucel M

Soluble in many organic solvents, such as ethyl alcohol and acetone, and soluble in water below 38°C, but insoluble in water above 45°C, characterized by a viscosity of 400:150mPa, with a concentration of 2% in water at a temperature of 25°C. It has a viscosity of 400:75mPa, with a concentration of 2% in ethanol at 25°C [13–16].

Methyl trimethoxy silane (MTMOS)

It is a colorless liquid with a strong smell that has a boiling point of 100°C and has a blinking temperature of 8.3°C and has no explosive properties. With trade name: Dow Corning(R) Z 6070 Silane Reach, Registration Number: 01-2119517436-40. Chemical name is: Alkoxysilane has a viscosity degree: 1 CSt at 25°C and specific density: 0.948 g/cm^3.

It is one of the oxyl-coxy-silane compounds that are used in strengthening the building materials due to its low partial weight, low viscosity, and good permeability. The polymer, as it penetrates to several centimeters in the pores of the material, may be used on the surface that contains a high percentage of moisture. Gonorrhea compounds may be ineffective in giving the surface of the material a protective surface layer if this surface is spread by the salts as these salts reduce the effectiveness of cohesion. This substance can be used without any solvents, and the soluble B72 solute in toluene may be added to improve its properties and chemical formula $(CH_3)SiOH$ [16–19].

The success of using this compound in isolating surfaces against moisture sources and strengthening the surface layers is since the hydroxyl alkyl compounds silane in water form a silicon resin that contains two or three intersecting bonds between silicon and oxygen, in addition to that each silicon atom in the molecule carries the alkyl group [18–21].

Methods

The stiffening material was applied using the spray method as in figure 2, because the archaeological samples are very weak and have a scaly surface and very weak, so we find that the spray application is very suitable with weak fragile surfaces and to ensure good penetration of the stiffening material into the pores of the stone.

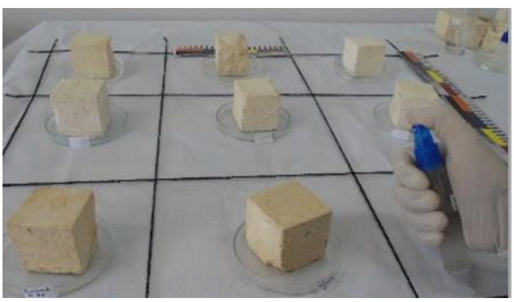


Fig. 2. The application of the consolidation materials using spray

In which limestone samples were fortified with the consolidation materials with different concentration ratios, then a drop of water was placed on the surface of each reinforced limestone specimen in order to measure the time needed to absorb the water drop and know the best reinforcement material that proved successful in the consolidation process as in figure 3.

Fig. 3. The stone samples absorbing the water drop

The first experiment

In the first experiment, the stone samples were strengthened with the strengthening materials with different concentration ratios and spraying was applied once and measuring the time required for water drop absorption as shown in Table 1.

The second experiment

In the second experiment, the stone samples were strengthened with the strengthening materials with different concentration ratios. The application was sprayed twice and measured the time required for water drop absorption as shown in Table 1.

The third experiment

In the third experiment, the stone samples were strengthened with the aforementioned strengthening materials with higher concentration rates than the first and second experience, the spray application increased to three times, and the time required for absorption of the water drop was measured as shown in Table 1.

Fourth experiment (Absorption by capillary action)

In the fourth experiment, the stone samples were strengthened with the aforementioned strengthening materials with different concentration ratios and the spray application increased to four times .The reinforced limestone samples were immersed in Petri dishes filled with water (30 million cubic meters) in order to measure absorption by capillary property and measure the time required for absorption and to know the best consolidation material proved successful in the process of strengthening as shown in figure 4 and in Table 1 [21–24].

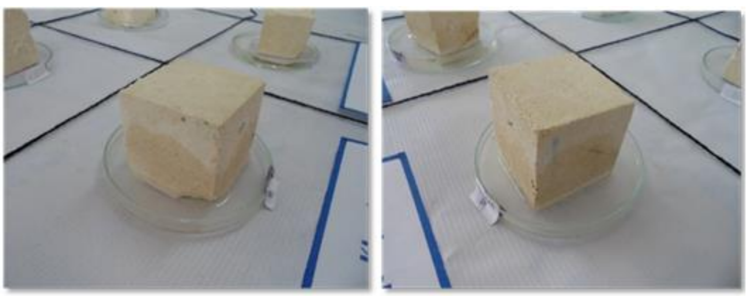


Fig. 4. Limestone water absorption

Table 1. Parameters of the experiments

The name of the material	Concentration of materials (%)	The number of times sprayed	Absorption time (min)
Experiment 1			
Paraloid B 72	3	1	5
Klucel G	3	1	0.5
MTMOS	As it is liquid	1	80
Experiment 2			
Paraloid B 72	3	2	10
Klucel G	3	2	3
MTMOS	As it is liquid	2	156
Experiment 3			
Paraloid B 72	5	3	275
Klucel G	3	3	30
MTMOS	As it is liquid	3	188
Experiment 4			
Paraloid B 72	5	4	4
Klucel G	3	4	0.25
MTMOS	As it is liquid	4	7

Fifth experiment

Archaeological samples of limestone were strengthened cubes 3cm x 3cm with consolidation materials by spraying Paraloid B-72 with a concentration of 3% twice and 5% once as in previous experiments, Klucel G with a concentration of 3% 3 times, MTMOS 3 times [25–27].

After that, the samples were placed in dishes where the saline solutions were used for one salt cycle (Sodium Sulphate with a concentration of 15%, Sodium Chloride with a concentration of 15% as shown in figure 5 [28]. After absorbing the strengthened samples of the brine and evaporating the water, the salts began to bloom on the surface of the stone as shown in Table 2 and 3 [29].

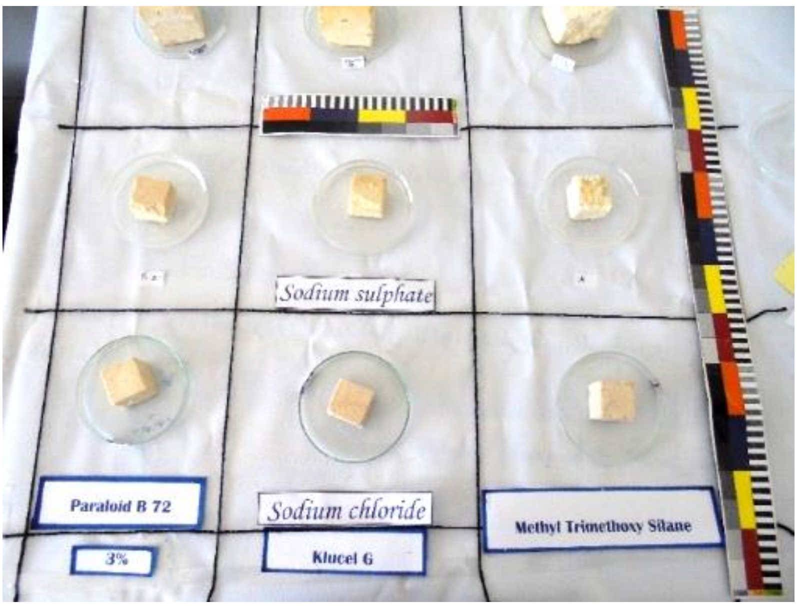


Fig. 5. The reinforced stone samples in the saline solutions

Table 2. Pictures and shapes blooming and the formation of salts on the surface of stone samples

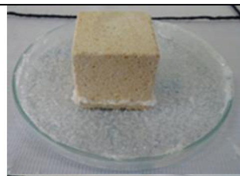
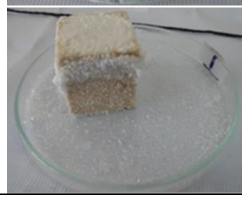
The name of the material	Sodium Sulphate	Sodium Chloride
Paraloid B 72		
Klucel G		
MTMOS		

Table 3. Pictures showing the blooming and formation of salts on the surface of stone samples using the Digital Microscope

The name of the material	Sodium Sulphate	Sodium Chloride
Paraloid B 72		
Klucel G		
MTMOS		
		

Evaluating the consolidation materials using physical and mechanical tests

After the completion of the strengthening operations, it was necessary to measure the physical and mechanical properties of the stone samples before and after the application to know the change that occurred to the stone granules and the extent of the success of the chemicals in the strengthening and compare the results to reach the best materials used for penetration inside the stone granules and their success in the strengthening process [29–33].

Physical Properties Test

Density test

The density of the stone samples was measured before application (the standard sample). The density of the stone samples was measured after applying the stiffeners to identify the change that happened to the stone samples as shown in Table 4.

Table 4. Density test

The sample	Density (g/cm^3)
Standard sample	1.983
Paraloid B 72	2.2
Klucel G	2.368
MTMOS	1.998

Water absorption test

In this test, the samples were dried in drying ovens for 48 hours, after which they were weighed after drying. The samples were then placed in the water for 48 hours and then weighed after absorption. After that, the absorption ratio was measured by the following equation: Absorption ratio = (weight after absorption - dry weight)/dry weight × 100 [33–36].

Table 5. Water absorption test

The sample	Dry weight (g)	Weight after absorption (g)	Absorption ratio (%)
Standard sample 5 × 5	255	280	**9.8**
Standard sample 3 × 3	57	63	10.53
MTMOS	248	250	**0.8**
Paraloid B 72	274	292	6.6
Klucel G	295	324	9.83
MTMOS+ Na_2SO_4 3×3	64	67	4.68
MTMOS+NaCl 3×3	68	69	1.47
Paraloid B72+ Na_2SO_4 3×3	64	66	3.12
Paraloid B72+NaCl 3×3	63	67	6.35
Klucel G + Na_2SO_4 3×3	61	64	4.91
Klucel G +NaCl 3×3	68	69	1.47

Mechanical properties test (Compressive strength)

The durability of the stone specimens of pressure (the standard sample) and the stone samples were measured after applying the stiffness to measure the extent of the strength of the specimen's stress for the pressure on them and to reach the best chemicals that gave the stone the high durability of the pressure and the bonding and consistency of the stone granules as shown in figure 6 and Table 9 [36–40].

Fig. 6. Shows the selection of pressure for samples

Table 6. Compressive strength

The sample	Pressure bearing strength (kg)	The sample sizes (cm^2)	The ratio (kg/cm^2)	The change in pressure ratio of the sample 5×5 (%)	The Change in pressure ratio of the sample 3×3 (%)
Standard sample	325	5×5	13	100	
Standard sample	240	3×3	26.7		100
MTMOS	**2860**	5×5	**114.4**	880	
Paraloid B 72	955	5×5	38.2	293	
Klucel G	548	5×5	21.92	168	
MTMOS+Na_2SO_4	350	3×3	38,9		145
MTMOS+NaCl	370	3×3	41,1		155
Paraloid B72+ NaCl	376	3×3	41,8		156
Paraloid B72+ Na_2SO_4	435	3×3	48,3		180
Klucel G+ Na_2SO_4	205	3×3	22,8		75
Klucel G+ NaCl	412	3×3	45,8		171

Results and discussion

First, second and third experiement

As shown in the Table 1 we find that MTMOS gave the best results in the previous three experiments, and it progressed in the absorption of a drop of water in a time capacity of 80 minutes, then 156 minutes, then at the end of 188 minutes as shown in figure 9, which indicates the extent of its success in the strengthening process.

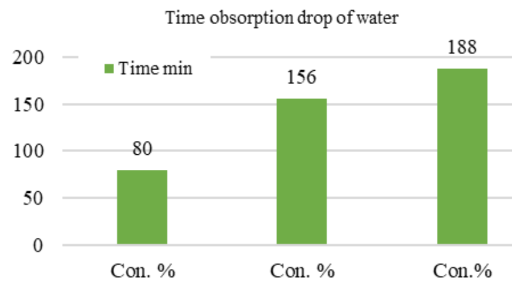


Fig. 7. The time required to absorb the water drop after the strengthening process with MTMOS the strengthening process with Paraloid B 72

As for Paraloid B 72, we find that it gave somewhat good results, as it ranged from 5 minutes, then 10 minutes, at a concentration rate of 3%, then 275 minutes as shown in figure 10, by increasing the concentration percentage to 5%. As for the material Klucel G, we find that it gave the least results of absorption of the water drop in a time of 0.5 minutes, then 3 minutes, then at the end of 30 minutes as shown in figure 9, which indicates that it did not give the desired results for consolidation.

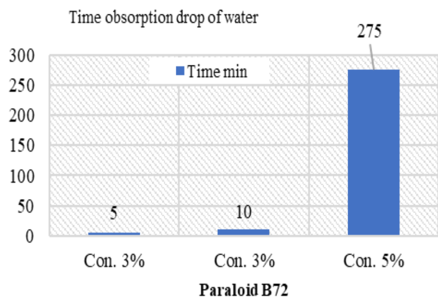


Fig. 8. The time required for absorption of a drop of water after

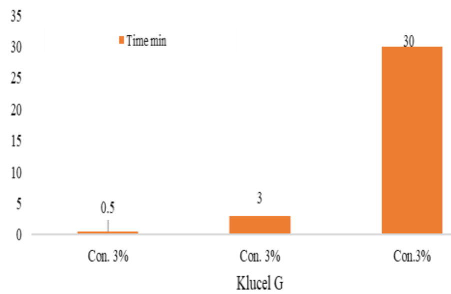


Fig. 9. The time required to absorb the water drop after the strengthening process with Klucel G

Fourth experiment Absorption by capillary action

As shown in the previous Table 1, we find that the substance MTMOS has given the best results, it took 7 days to absorb the amount of water, which indicates the extent of its success in the strengthening process as in the following figure 12, as for Paraloid B 72, we find that it absorbed the amount of water within 4 days, unlike Klucel G, which absorbed the amount of water in only 6 hours, which indicates that it did not give the desired results for the strengthening process.

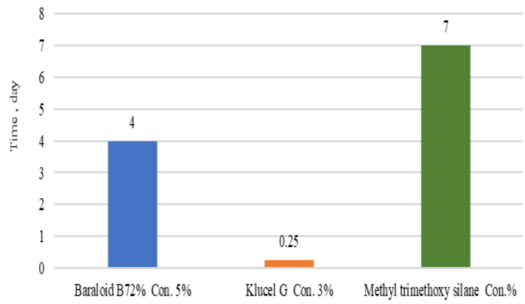


Fig. 10. Showing the time required for water absorption by capillary action

Physical and mechanical tests

Density test as in the previous Table 4, we find that the MTMOS material gave the best results 1.998g/cm^3, as the density of the sample after strengthening was not different from the density of the standard sample1.983g/cm^3, unlike Paraloid B 72 and Klucel G in which the density in them exceeded the standard sample.

Water absorption test

As in the previous Table 5, we find that the sample strengthened with the substance MTMOS gave the best results, which is the lowest absorption rate of water 0.8%, which indicates the extent of penetration in the pores of the stone and filled it with the reinforcement material as the standard sample gave a absorption rate of 9.8% as in the following diagram No. 5. While we find that Paraloid B72 gave 6.6% absorption, followed by Klucel G which gave a high absorption rate of 9.83%, which indicates a lack of good penetration of the booster material into the pores of the stone and the presence of voids and pores that were filled with water and consequently the failure to achieve the desired results from the booster process.

In the case of samples with salts, we find that the absorption rate has decreased from the standard sample to varying degrees, so in the case of salts in the samples strengthened with MTMOS, the absorption rate has decreased from 10.53 to 4.68% and 1.47%. In the case of samples strengthened with Paraloid B72 and with salts, we find that the absorption rate has decreased from the standard sample from 10.53 to 6.35% and 3.12%. In the case of samples fortified with Klucel G and with salts, we find that the absorption rate has decreased from the standard sample from 10.53 to 4.91% and 1.47%.

Compressive strength

As in the previous Table 6, we find that the MTMOS material gave the best results, as it has endured a pressure force of 2860kg, at a rate of 114.4kg/cm^2 compared to the standard sample, which gave a pressure bearing strength of 325kg at a rate of 13kg/cm^2 as shown in the following figure 11, which indicates the extent of its success in the strengthening process.

While we find that Paraloid B72 and Klucel G gave a pressure bearing strength of 38.2, 21.92kg/cm^2 compared to the standard sample that gave a pressure bearing strength of 13kg/cm^2

As for the samples fortified with reinforcement materials and with salts, we find that the pressure ratio has exceeded the standard sample with a few percentages varying from one salt to another as shown in the following figures 12 and 13.

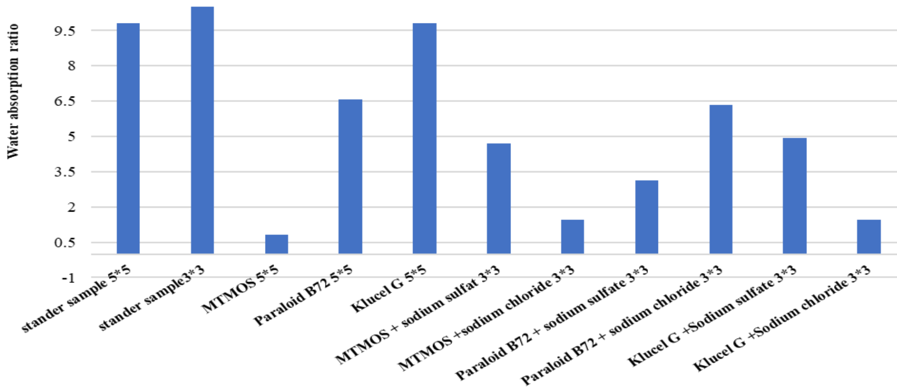


Fig. 11. The results of the water absorption test

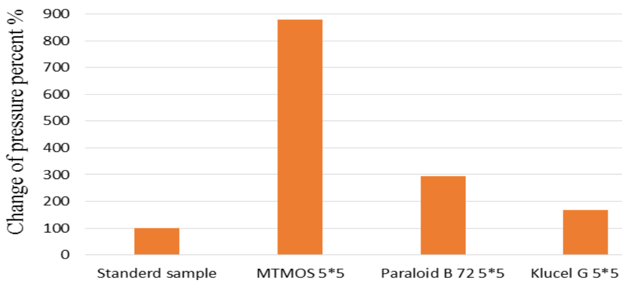


Fig. 12. The change in the pressure ratio in percentage of samples 5×5

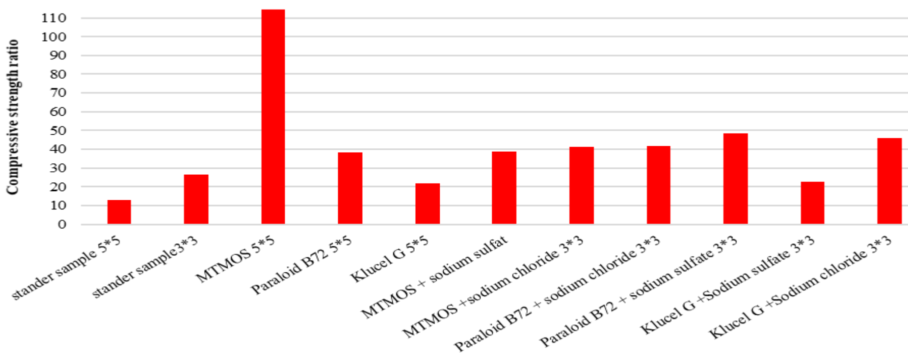


Fig. 13. The results of the pressure test for stone samples after the strengthening process

Evaluation the consolidation materials using the scanning electron microscope

The scanning electron microscope is considered one of the most important modern scientific devices used in the field of antiquities, especially the field of restoration. It provides us with stereoscopic images with a magnification force of 100,000 times. The examination is done on very small samples on the external surface of the sample and therefore it is not damaged by archaeological samples [40–44]. The scanning electron microscopes gives us three-dimensional images of different magnification power that appears and show all the fine details inside the samples to be examined to show all aspects of damage and different reinforcement materials, which helps in the success of the restoration process [44–49].

The scanning process was done using an electronic brand scanner JEOL- JSM-5400LV SEM - JEOL - JFC-1100E ion Sputtering Device (Fine Coating) The sample is prepared by gluing it from both sides with carbon material with six carbon or silver dough and then it is covered or coated with a thin metal layer such as gold until the surface is a good electrical conductor

Electrically Conductive and the thickness of the gold layer is between 20:20 angstrom.

The previous archaeological limestone samples that were reinforced by previous reinforcement materials were examined to clearly identify the extent of the damage suffered by the archaeological samples, as well as evaluating the reinforcement materials used to know the best and most appropriate in the process of strengthening.

The microscopic examination revealed that:

The extent of the deterioration, deterioration, and disintegration of limestone grains, with voids, gaps and cracks between the grains as shown in figures 14 and 15 of the standard sample.

The extent of the success of the MTMOS material in the strengthening process, and we find through the images the coverage or packaging of the reinforced material for the granules, the bonding and cohesion of the granules with each other, as well as the filling of the cracks in the reinforcement material as shown in figures 16, 17 and 18.

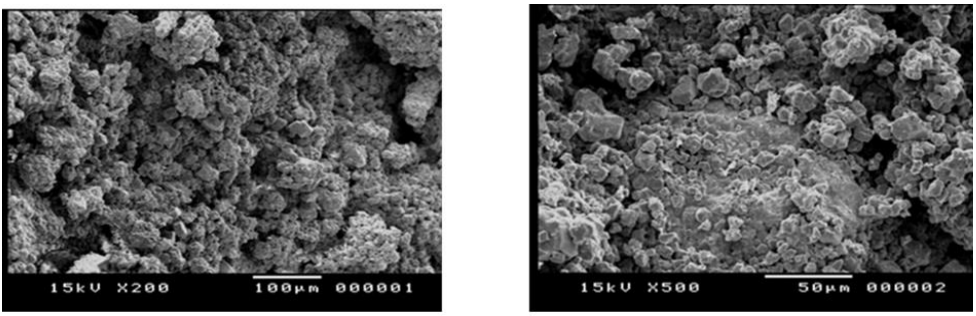


Fig. 14. Shows the disintegration of the grains, voids and gaps between the pores of the stone

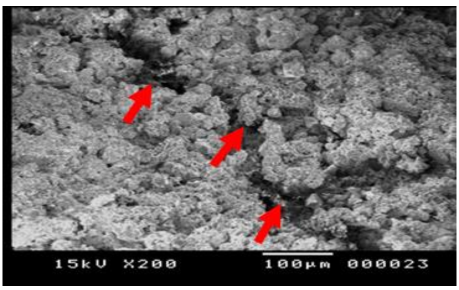


Fig. 15. The cracks between the pores of the limestone

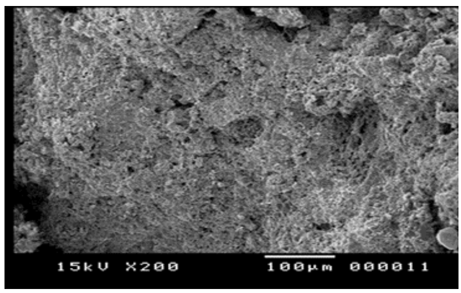


Fig. 16. The spread of MTMOS material between limestone granules in the form of a mesh or a protective film

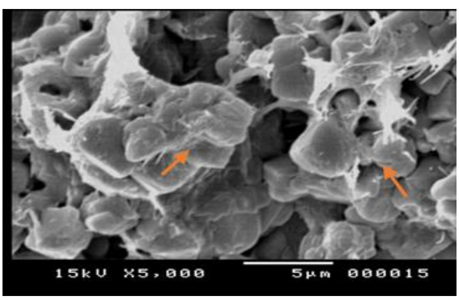


Fig. 17. The packing and covering of the granules with the MTMOS consolidation material

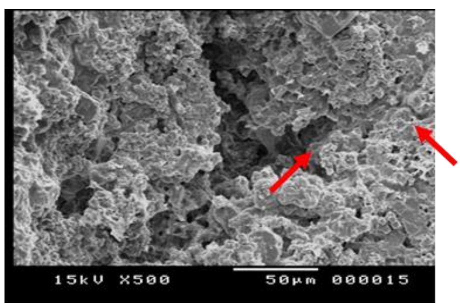


Fig. 18. The cracks are full of the MTMOS consolidation material

Klucel G material did not give the desired results from the strengthening; we find through the pictures that the reinforced substance does not cover the granules completely with the presence of voids and not all pores are filled with the strengthening substance as shown in figures 19, 20 and 21.

Paraloid B72 substance, we find that it did not give the desired results because it did not completely cover or cover the granules with the reinforced substance with the presence of gaps and voids between the grains, unlike the MTMOS substance that completely covered the granules as shown in figures 22, 23 and 24.

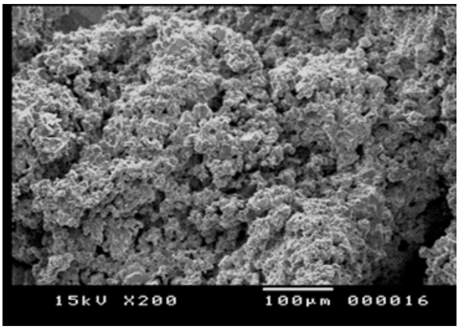


Fig. 19. Klucel G is not completely covered with granules

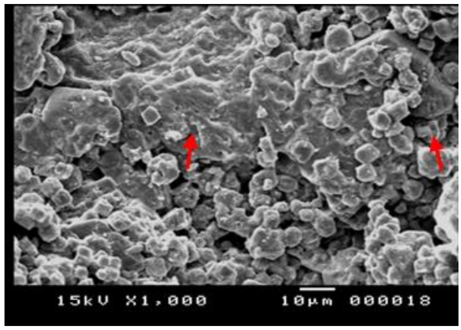


Fig. 20. The presence of granules that are not coated with Klucel G

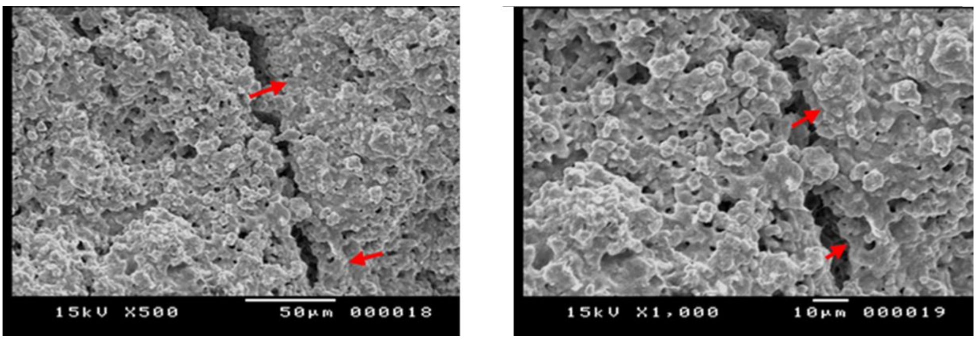


Fig. 21. Cracks not filled with Klucel G

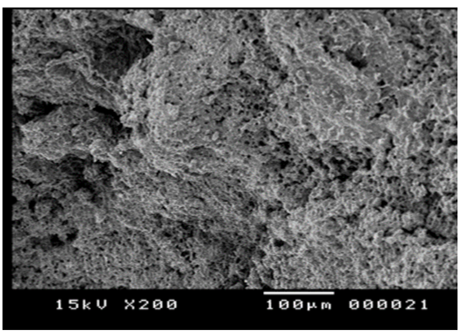


Fig. 22. The spread of Paraloid B72 inside the limestone pores

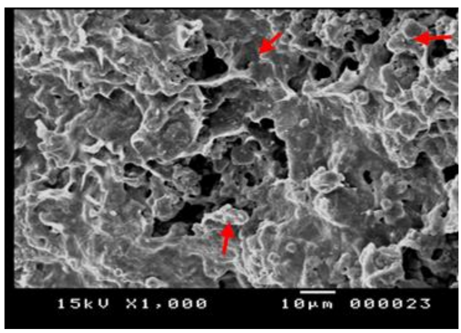


Fig. 23. The non-proliferation of Paraloid B72 booster material with blanks and gaps

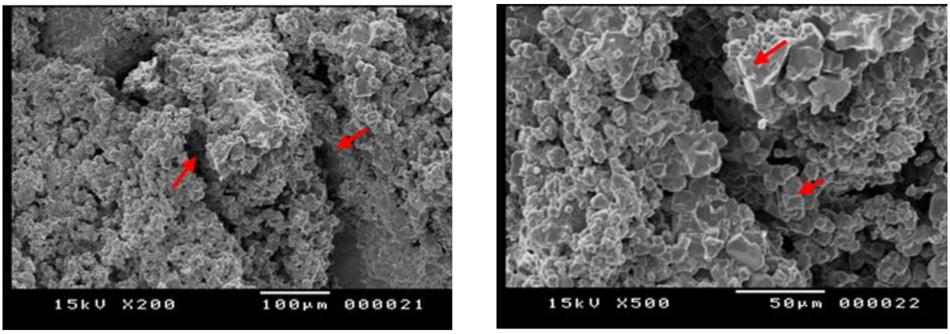


Fig. 24. The cracks are not filled with the Paraloid B72

In the case of samples strengthened with MTMOS and containing salts, we find that the salts are flowering over the coated granules and covered with the reinforced material and not penetrating the protective or reinforced film of the granules as shown in figures 25 and 26.

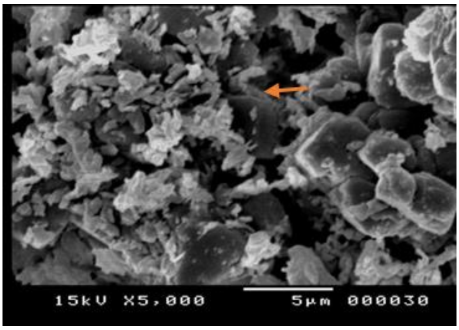


Fig. 25. The formation and flowering of sodium sulfate salts on the membrane of the reinforcing material MTMOS coated for the sample granules

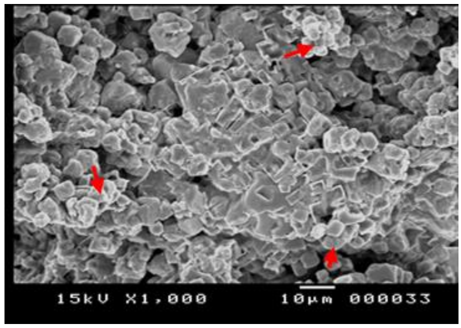


Fig. 26. The formation and flowering of sodium chloride salts on the membrane of the booster material MTMOS coated for the sample granules

In the case of the samples strengthened with Paraloid B72 and Klucel G, in which the salts are found, the salts are formed and blooming within the pores and between the grains, with a lot of voids and voids and tearing of the protective or reinforced membrane or envelope of the grains as shown in figures 27-30.

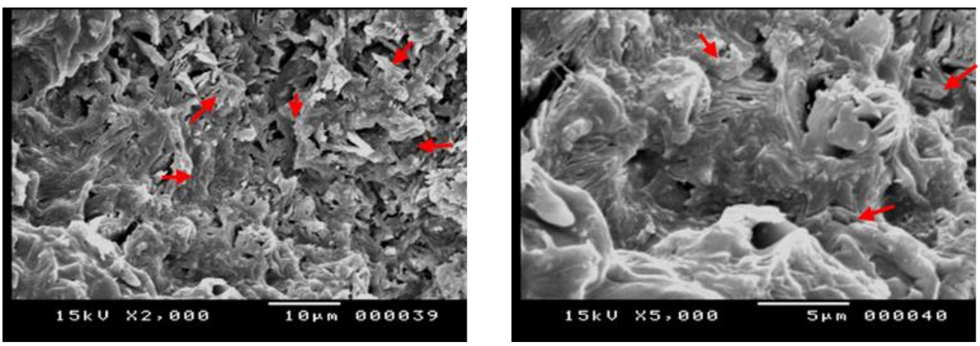


Fig. 27. The formation and flowering of sodium sulfate salts directly above the granules, having the film coated with Klucel G

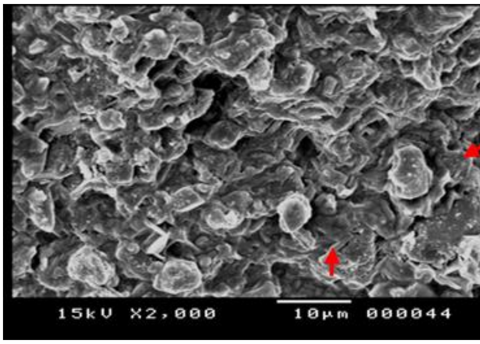


Fig. 28. The crystals of sodium chloride salts inside the pores of Klucel G

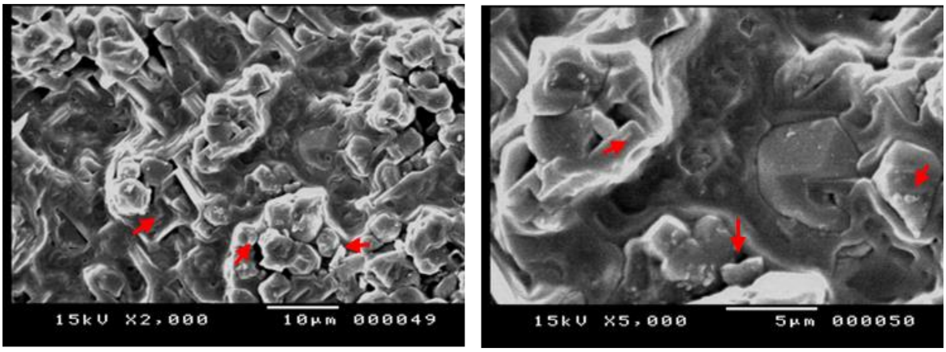


Fig. 29. The formation and flowering of sodium sulfate salts inside the pores and granules of Paraloid B72

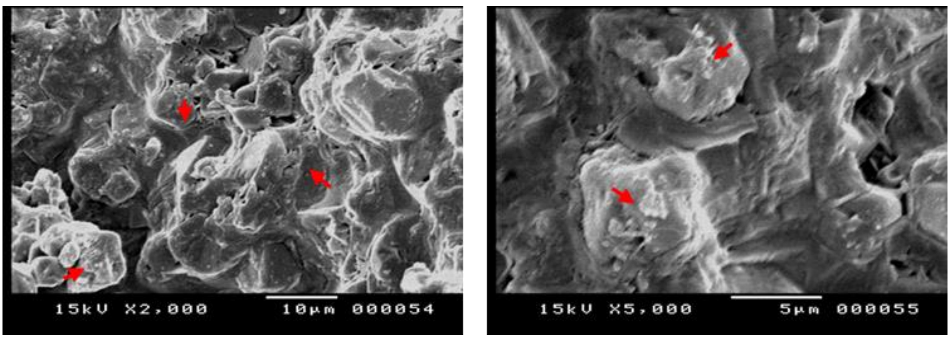


Fig. 30. The formation and flowering of sodium chloride salts inside the pores and granules of stone reinforced with Paraloid B72

Conclusions

The damage of stones and historical buildings is a serious problem that threatens the preservation of the world cultural heritage. Therefore, we find that all countries of the world are trying hard to continuously search and conduct chemical scientific studies to reduce the risk of different weathering factors and discover the best chemicals used in strengthening, restoration and treatment to preserve the architectural monuments, sculptures, and wall paintings etc. in this study, three types of consolidates materials were applied, which are (MTMOS), Paraloid B 72 and Klucel G, and the study showed that methyl tri-misoxy-silane(MTMOS) is the most suitable and It is better to strengthen the archaeological stone samples in the current situation, and an improvement in the properties of the stone has been shown, therefore scientific studies and research in the field of restoration and maintenance of antiquities and the improvement of the properties of stones must not stop in order to reach the ultimate goal of preserving the holdings of the world cultural heritage from stones and historical and archaeological buildings To remain for many years for future generations.

Acknowledgments

The authors would like to thank the employees of the El-Ashmunein archaeological area, Minia, Egypt, and to thank the members of the archaeological mission in the Tuna Al-Jabal Archaeological Zone in Minya, Egypt (Minia University in Egypt - Hildesheim University, Germany) for assistance in conducting the research. The authors wish to thank DOW CORNING, USA, and UNIVAR EGYPT LLC, Egypt for their assistance in accomplishing my experimental aspect of the research.

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Received: September 16, 2020
Accepted: October 4, 2021