

THE EFFECTIVENESS OF NANO MATERIALS AND NANO-MODIFIED POLYMERS FOR PRESERVATION OF HISTORIC BRICK MASONRY IN RASHID, EGYPT

Sayed HEMEDA^{1*}, Mervat KHALIL², Ahmed SHOEB¹, Ahmed Abd EL AZIZ¹

¹Conservation Department, Faculty of Archaeology, Cairo University, Giza, Egypt (P.O 12613).

²Building Physics Institute, Housing & Building Research Center, 87 El Tahrir St, El-Dokki, Giza, Egypt.

Abstract

The Rosetta, (Rashid City) of Egypt is considered the second-largest open-air museum after Cairo city. Historic brick masonries are exposed to aggressive environmental and geotechnical conditions especially the ground water rise factor. The building materials in the historic buildings in this city are suffered from many factors and forces of damage and instability, which caused the structural and out of plane deficiencies. Al-Mahalli mosque is considered the largest central mosque in the city is threatened of damage and structural problems as a result of mechanical, physiochemical and biological deterioration factors. From the mosque survey we found that the ground water, salt weathering, rain as well as earthquake, vibration levels, pollution and human damage factors are the most important ravages that threaten the ancient buildings in rational overall domestic and mosque in particular. The assessment of the current state and the development of appropriate restoration strategy were performed including the analytical study of the main construction materials. The pilot study was performed on samples of fired bricks using some traditional protective and consolidating materials as well as some nano materials to choose the best one in the treatment and maintenance of historic fired brick. The evaluation methodology is performed using a set of stress analysis of the treated specimen processed and compared with non-treated or standard samples that were not exposed to the processors, as well as appoint resistant of red bricks using the ultrasonic velocity test PUNDT also the physical properties of the samples including the micro porosity and finally using the scanning electron microscopy (SEM) and polarizing light microscopy (PLM) to investigate the treated samples. The results proved the superiority of the samples that have been strengthened by nano silica concentration of 1.5% and nano titanium concentration of 1.5% with Wacker Bs15 concentration in 20% with water, which was given the code (J).

Keywords: Rashid; Mechanical properties; Physical properties; Red bricks; Nano materials

Introduction

Brick masonry structures of architectural heritage built with fired bricks and mortars in Rashid city constitute a significant part of world cultural heritage. Their preservation implies high cost restoration projects and interventions with appropriate materials and techniques with respect to the values and authenticity of the monumental structure.

Bricks and mortars are the fundamental building materials of these historic structures and their behavior to salt enriched environment can present differences. When the conditions which adjust the solution supply and the evaporation rate are stable a steady system may develop. High evaporation rate often means that salts crystallize on the material's surface. Soluble salts

* Corresponding author: hemeda_200x@yahoo.com

crystallization in the porous structure of a stone is considered to be one of the most important reasons for decay due to the mechanical volumetric expansion of salts which causes stresses and due to the chemical action as salts may cause dissolution of mineral admixtures.

The historical and archaeological heritage of any nation is a mirror that reflects what passed on this nation of social, environmental conditions. Therefore, it is very important to maintain the structural elements of this historical and archaeological heritage. In Rashid, the fired brick masonry buildings are exposed to many deterioration factors and damage forces that cause the damage and degradation, especially salty ground water, which is the link between all the other damage factors in historical buildings, as they play an important role in determining the effectiveness of some of the other ravages [1].

The ground water is the most important source of quick impact on construction materials including red bricks. Rashed city is bounded by the Mediterranean Sea to the north and a branch of the Nile Rosetta from the east and Lake Adco from the West. This site leads the water fluctuations land between rise and fall which made the continuing wetness and drought for the foundations and walls of operations [2].

The ground water containing different types of dissolved mineral salts in which they are the most important physical weathering and destructive processes that affect porosity building materials and other physical and mechanical properties [3]. The dark spots and salt efflorescence on the surfaces of red bricks in the ancient buildings identified the ground water effect on it. Rain will considered one of the damage factor affecting the monumental buildings materials in rational factors, where salts hydration and crystallization after the drought weakness the internal structure of these materials [4-6].

These salts generate internal pressure could lead to cracks in the fabric of building materials, especially red bricks and turn it into a powder and lost parts of it [7]. The change in temperature range is an important source of pressures on building materials, where we note flake and segregations minute cracks in red bricks in many archaeological buildings in Rashid [8].

Air pollutants also contribute significantly to the occurrence of serious damage to archaeological establishments in Rosetta in which they lead to erosion of construction materials and composition of the black crust on the surface, which largely leads to the distortion of surfaces as well as stimulate chemical weathering processes for metal components of these materials [9] Wind movement transferred and deposited these contaminants on the surfaces of archaeological materials [10].

The earthquakes affected a large variety of structural systems. The severity of damage is a function of the structural type, quality of workmanship, material, and local soil conditions [11].

Observations of the damaged areas close to the epicenter of the Dahshour earthquake (Cairo indicated that they can be rated VII on the Modified Mercalli intensity (MMI) scale with an estimated peak ground acceleration of about 10% g, [12]. The Rosetta, Egypt is considered the second-largest open-air museum city after Cairo city. Historic brick masonries are exposed to aggressive environmental conditions especially the ground water rise. The building materials in the heritage buildings in this city are suffered from many damage factors and the forces of damage and unbalance, which caused the damaged. Al-Mahalli mosque is considered the largest central mosque in the city is threatened damaged and structural deficiency as a result of mechanical and physiochemical and biological factors.

Figure 1 presents the layout of Al Mahalli mosque and Figure 2 shows the main and east facade of Al Mahalli mosque, under restoration and intervention processes.

Figure 3 show the main and east façade of Al Mahalli mosque, the effect of ground water on the mosque, Main entrance of the mosque and the damage effect on it, the vertical cracks and observed deformations in the structure of mosque and other buildings. Also the living organisms have a role of damage circle that attacked the building materials in ancient buildings in rational because the environment is suitable for the growth of these objects and gravity as produced from

organic acids and inorganic as well as deformation chromatography to external surfaces of building materials due to the production of various fungi colors [13].

Hence, it was necessary to use the achievements of other sciences as physics and chemistry of the significant results can be adapted and utilized in the treatment and maintenance of archaeological materials. Given the growing interest in recent times with the knowledge of nanotechnology and in view of the achievements of this technology from the success and progress in improving the properties of materials in general and indicated by recent research on the principles for nanotechnology in construction areas and building materials, which stressed the importance of the use of nanomaterials applied to protect the facades of historical buildings as well as its role in the architectural restoration operations [14]. Hence nano materials can be adapted in the treatment and maintenance of red bricks, a basic building material in ancient buildings in Rashid.

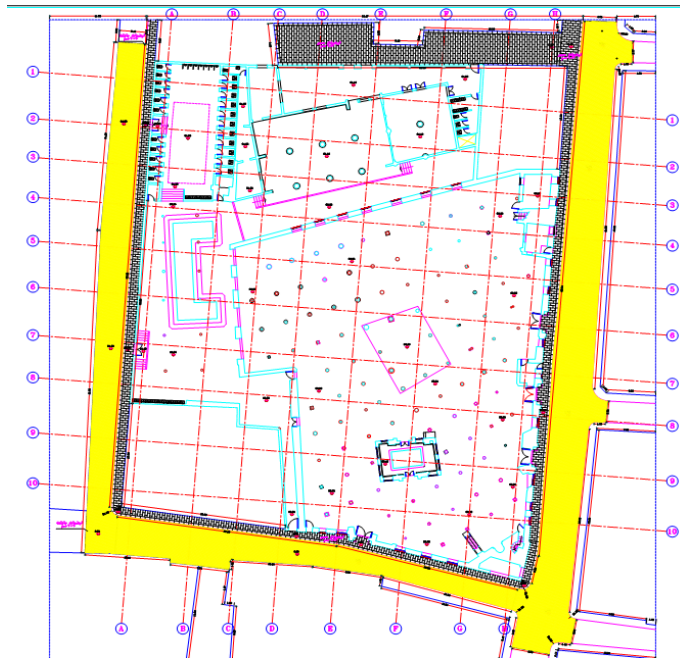


Fig. 1. The layout of Al Mahalli mosque in Rashid city, Egypt (the applied study)



Fig. 2. The main and east facade of Al Mahalli mosque, under restoration and intervention processes.



Fig. 3. Deterioration issues: a - Ground water rise inside Al Mahalli mosque; b - Deterioration due to rising humidity; c - Major arcades and the overhanging structure. cracks and fissures in the vertical walls; d - The main facade of El Manadily house, dangers cracks appeared in some pillars and separation between the façade and the radial walls; e - El Manadily house, deformation of the brick in the zone of the borders and main wall of the facade

Methods and Materials

X-ray diffraction test method was carried out on fired bricks samples from the right side of the main entrance of the east façade of the mosque. XRD technique using a PW1050/70 diffractometer (Philips, Holland) was recorded with a diffractometer with Cu-K α radiation generated at 40kV and 40mA. It covers 2θ from 5° to 50° . The diffractometer shows that this sample composed of Quarts, Hematite, Calcite and Halite by large ratio with a small amount of Albite and Mullite.

Scanning Electron Microscope (SEM) model Inspect S (FEI Company) was used to investigate and analysis the red brick sample (control sample; U). The microscope machine was equipped with an energy dispersive X-ray analyzer (EDAX).

Polarizing Light Microscope, a N.Kon Eclipse LV 100 PoL was used for investigation.

Sample Preparation

Al-Mahalli mosque in Rashid city was chosen for this study. Studying the site of this mosque found that the main building materials are the fired bricks. Collected number of fired brick fragments throw on the ground due to the distortion of some parts of the wall and architecture elements which exposed to ravages factors in this site. The specimens were cut to cubes of $5 \times 5 \times 5$ cm, and then dried in electric oven for 24 hours at $100 \pm 5^\circ\text{C}$. 33 specimens were

prepared and divided to 11 groups each group of code name composed of 3 specimens. Figure 4 shows the specimens with their code number before the consolidation treatment.

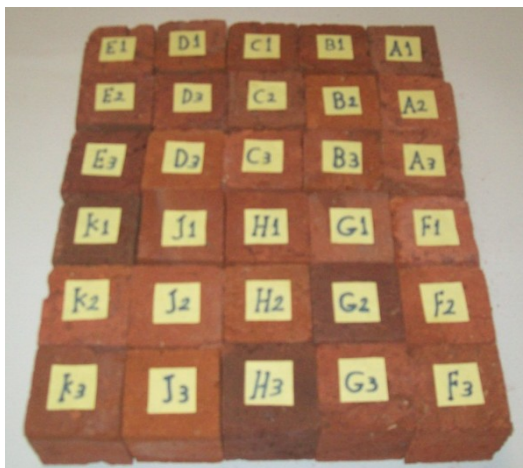


Fig. 4. Specimens with their code number before the consolidation treatment

Consolidation material used

Consolidation process required one of the important proceed to valid coherence for the internal structure of the fired bricks in historic buildings in Rashed city. Consolidation material takes into consideration its ability to improve the physical and mechanical properties and it’s compatible to the nature of fired bricks fabric. The materials were used as follow in table 1.

Table 1. The traditional and nano materials used for consolidation

Traditional materials	Nano-materials
Waker BS 15	Nano silica
Waker SKM 550	Nano-titanum
Estel 1100	Nano calcite
Euco Colle	-

In case of single shape (nano granule dispersed in carrier media such as water or alcohol), these materials made one or more job. For example nanosilica used in strengthened the mortar of lime [15, 16], and the form of gypsum materials repelled to water [17]. Nano-titanum used in strengthened of hydraulic mortar and improve the physical and mechanical properties of these mortars. In case of composed shape, one or two of nano materials were be mixed with polymer. The mixing must be good to get homogenous composed has good characteristics better than the single shape. Using nano silica and nano titanium mixed with polymer lead to improve and reinforced historical materials, improve also their mechanical properties and be super water repellent and self cleaning [18, 19]. The distributions of nano materials in polymer silicone and acrylic solution with a defiant concentration success in create protect layered for historical material surfaces. These layer characteristics by super water repellent and protect these materials from open environment which exposed to heavy rain and snoe and air pollution [20]. Nano reinforced materials applied with brushing, which appear the penetration, distribution and homogeneity through the historical materials [21]. This application used in 10 treatments. Treatment from 2-5 carried out by using the original materials (polymers), while treatment from 6-11 carried out by using nano materials in single or composed shape. Group one is the control sample.

Table 2 presents the consolidation materials used in each treatment.

Table 2. The consolidation materials used in each treatment

No.	Sample	The consolidation materials used
1	U	Control sample
2	A	Aclacrecol materials with 25% concentration in water
3	B	(Waker Bs15) Bs15 materials with 20% concentration in water
4	C	(Waker SKM 550) SkM 550 with 10% concentration in water
5	D	Estel 1100
6	E	Nano Silica with 3% concentration in alcohol
7	F	Nano Silica with 2% concentration in (Waker Bs15) Bs15 materials with 20% concentration in water
8	G	Nano restore with 50% with Aclacrecol materials with 50% concentration and diluigh in water by 1;1 ratio in water
9	H	Nano Titanium with 2% in Estel 1100
10	J	Nano Silica with 1.5% concentration and Nano Titanium with 1.5% with (Waker Bs15) Bs15 materials with 20% concentration in water
11	K	Nano Silica with 2% concentration with (Waker SKM 550) SKM 550 with 10% concentration in water

Results and discussions

Table 3 shows the percentage chemical compounds of fired brick sample.

Table 3. The percentage chemical compounds of fired brick sample

Minerals	Chemical symbol	Chemical compounds (%)
Quarts	SiO ₂	47.19
Hematite	Fe ₂ O ₃	19.54
Albite	NaAlSi ₃ O ₈	8.86
Halite	NaCl	7.33
Mullite	3Al ₂ O ₃ 2SiO ₂	11.9 7
Calcite	CaCO ₃	6.55

Figure 5 shows Photograph of red brick sample (control sample; U). The sample examined by SEM and EDAX shows that it composed of Si, C, Na, Al, Cl, Fe, Ca, Mg, K, Ti, S, P and O. Table 4 shows the chemical analysis by EDAX for the control sample.

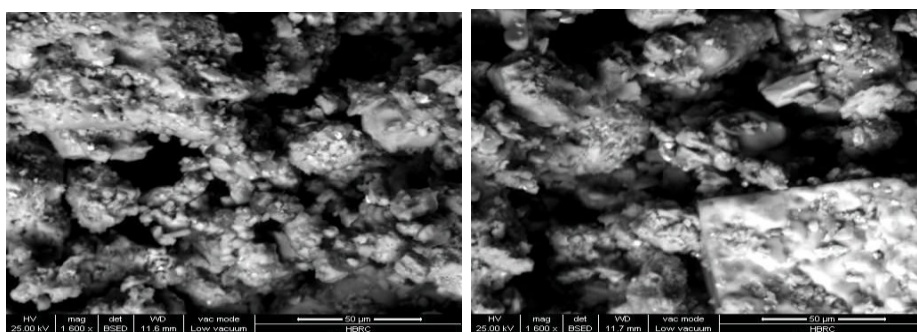


Fig. 5. Micro structure of fired brick (control sample; U)

Table 4. The chemical analysis by EDAX for fired brick (control sample; U)

Main Constituents	SiO ₂	C	NaO ₂	Al ₂ O ₃	CL	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	SO ₃	P ₂ O ₅
Concentration (%)	17.79	7.17	6.63	6.38	6.21	5.33	3.01	1.73	1.46	0.76	0.55	0.21

Evaluation and Analysis for consolidation materials

Mechanical properties for consolidated or treated samples

Uniaxial Compressive Strength. Three Cubes samples of 5×5×5cm were used to carry out the compression test of the control and the modulated samples. Compressive strength carried out using 50 ton Italy Matest pressing machine with a loading rate of 6.5kN/min as the specimens. The pressure resistance (compressive strength) of each sample was calculated as follows in Equation 1,

$$C.S = P/A \text{ [kg/cm}^2\text{]}, \quad (1)$$

where: C.S is the compressive strength; in kg/cm², P load; in kg and A area, in cm²

Ultrasonic Pulse Velocity (PUNDT)

This test gives indication about the quality of building materials by the way of waves flow. The velocity of waves flow of ultrasonic through any materials depend on two factors, one of them is internal factor depend on the type of materials, grain size, the fabric, the density and porosity of the material. The other factor is external factor depend on the temperature, porosity pressure of liquid and the stress on materials. For this test an ultrasonic tester model E4b was used, in which it consists of two microphones for transmit and receive waves connected with the main device. The tow microphone put on both side of the specimen to determine the time of the wave travel. The velocity of the wave determined as follows in Equation 2,

$$VP = H (X1000)/T (X1000000), \quad (2)$$

where: H is the height of spaceman in meter; T is the time of wave travel in spaceman in min.

Figure 6a shows the average wave velocity for three samples for each group. The figure shows that sample with code number J treated with Nano Silica with 1.5% concentration and Nano Titanium with 1.5% with (Waker Bs15) Bs15 materials with 20% concentration in water, gives the highest velocity of 2334m/s which increase the control one by about 48.6% which is 1517m/s.

Physical properties

The physical properties (bulk density, water absorption and apparent porosity) of these samples were determined by calculating the volume of each sample, measuring the dry weight and the wet weight of each sample. The physical properties were calculated as follows,

Bulk Density (d) in g/cm³ was determine as follows in Equation 3,

$$d = W/V \quad (3)$$

where: d is the bulk density in g/cm³, W is original weight in g and V is volume in cm³

Water Absorption (W.A) in % was determine as follows in Equation 4,

$$W.A = \frac{W_2 - W_1}{W_1} \times 100 = \% \quad (4)$$

where: W.A is the water absorption in %, W₁ and W₂ is dry and wet weight in g.

Apparent porosity (A.P) in % was determine as follows in Equation 5,

$$A.P = \frac{W_2 - W_1}{V} \times 100 = \% \quad (5)$$

Where: A.P is the apparent porosity

Figure 6 show the physical properties of samples. Figure 6c shows the bulk density in which sample with code number J treated with Nano Silica with 1.5% concentration and Nano Titanium with 1.5% with (Waker Bs15) Bs15 materials with 20% concentration in water gives the highest bulk density of 1.64g/cm³ which higher than the control one by about 31.2% which was

1.25g/cm³. Figure 6d shows the water absorption in which sample with code number J treated with Nano Silica with 1.5% concentration and Nano Titanium with 1.5% with (Waker Bs15) Bs15 materials with 20% concentration in water, gives the lowest water absorption of 1.62% which lower than the control one by about 31.2% which was 28.14%. Figure 6e shows the apparent porosity in which sample with code number J treated with Nano Silica with 1.5% concentration and Nano Titanium with 1.5% with (Waker Bs15) Bs15 materials with 20% concentration in water gives the lowest apparent porosity of 2.64% which lower than the control one by about 31.2% which was 33.1%.

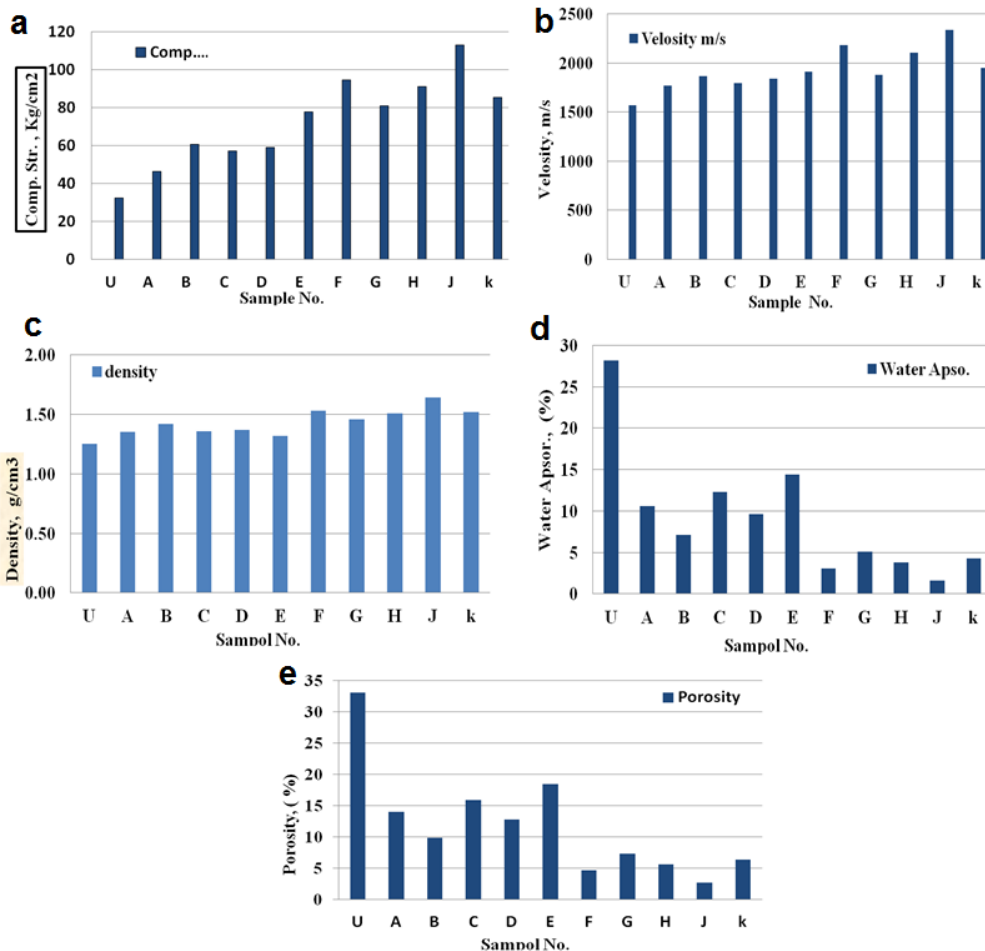


Fig. 6. The test results for the bricks: a - The average compressive strength of samples after consolidation; b - The average wave velocity of samples after consolidation; c - The average bulk density of samples after consolidation; d - The average water absorption of samples after consolidation, e - The average apparent porosity of samples after consolidation

SEM analysis after treatment

Scanning Electron micros for red brick after treatment were carried out using SEM with EDAX to investigate the effect of reinforced materials and its penetration through the texture of fired brick by comparing them with the untreated sample. Figure 7 show these investigation equipped with an energy dispersive x-ray analyzer (EDX).

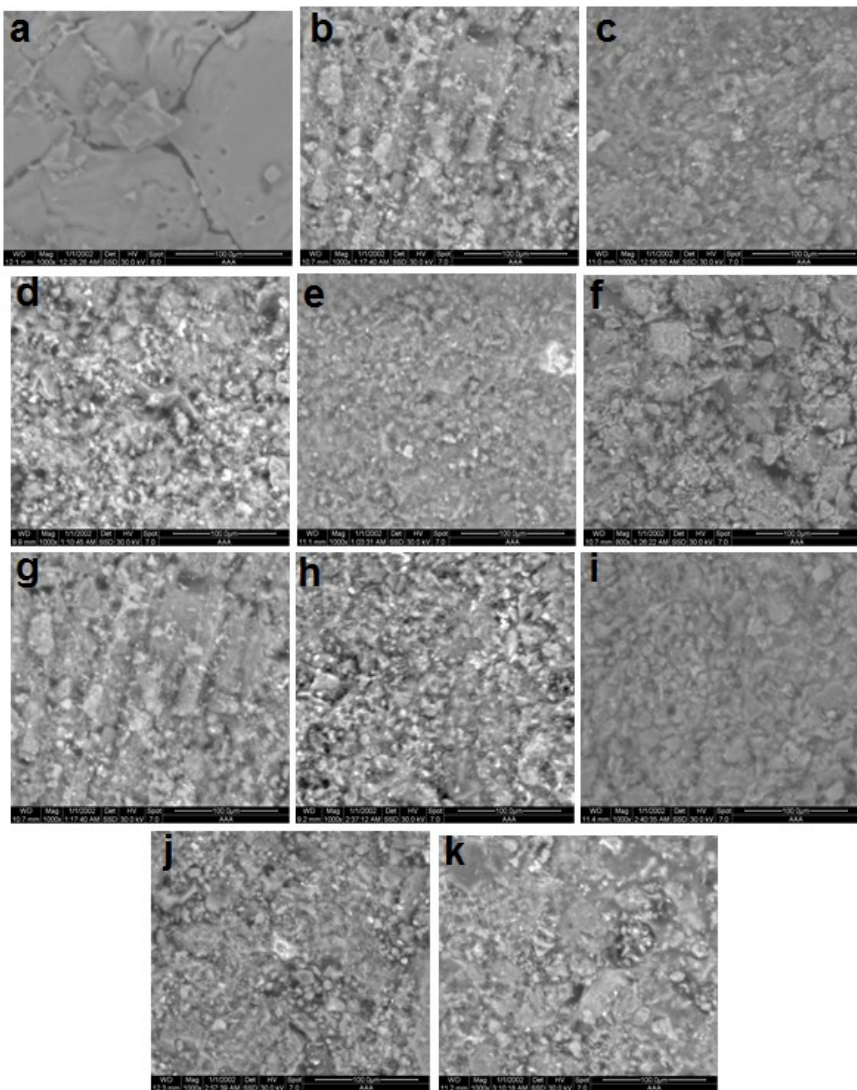


Fig. 7. SEM images with magnification 1000x for control and treated Samples by different methods

Control sample U, shows the weakness and cracks of the sample and also shows non cohesion and interdependence with the presence of some salt impurities (Fig. 7a). Sample A treated with acrylic materials with 25% concentration in water shows the complete distribution of polymer on sample surface and inside holes (Fig. 7b). Sample B treated with (Waker Bs15) Bs15 materials with 20% concentration in water shows the homogenous penetration and distribution of polymer and covering the grains without close the pore (Fig. 7c). Sample C treated with (waker SKM 550) SKM 550 in 10% concentration with water, shows the the non complete distribution of polymer on the surface of sample and so, the non cone connect of grains by good way (Fig. 7d). Sample D treated with Estel 1100 shows the presence of thick layer polymer which covers the grains by excellent way (Fig. 7e). Sample E treated with Nano Silica with 3% concentration in alcohol shows the good homogenous arrangement of nano silica particles but it is not able to cover all surfaces and so holes appear (Fig. 7f).

Sample F treated with Nano Silica with 2% concentration in (Waker Bs15) Bs15 of 20% concentration in water shows the good distribution and penetration for polymer and nano silica particles distributed with homogeneous and arranged shape (Fig. 7g). Sample G treated with Nano restore with 50% with acrylic materials with 50% concentration and diluigh in water by 1:1 ratio shows the good distribution for polymer but nano Restore particles distributed with non homogeneous shape (Fig. 7h). Sample H treated with Nano Titanium with 2% concentration in Estel 1100 shows the good distribution and penetration for polymer and covering the grains. Also nano titanium distributed with good arrangement on the surface (Fig. 7i). Sample J treated with Nano Silica with 1.5% concentration and Nano Titanium with 1.5% with (Waker Bs15) Bs15 materials with 20% concentration in water shows the exlent distributed and penetration for polymer on the surface and inside, without closing the pore. Also SiO_2 and TiO_2 particals distributed in arranged way on sample surface. This indicates the strength of sample and its ability of water retard (Fig. 7j). Sample K treated with Nano Silica with 2% concentration with (Waker SKM 550) SKM 550 with 10% concentration in water shows the good distribution of polymer, but SiO_2 distributed in semi-arranged way (Fig. 7k).

In figure 8 we have the main gate of Almahhali Mosque in Rashid before and after the restoration processes.



Fig. 8. The main gate of Almahhali Mosque in Rashid before and after the restoration processes.

Conclusions

The main important damage factors of historical building in Rashid are the ground water, rains, salts, variation of temperature, air pollution and biological factors.

XRD, Photographic analysis and SEM indicate that the red bricks of Rashid consists mainly of quartis with the precence of feldsbar, hematite, albite, halite, mullite and calcite

Nano-materials improve the physical and mechanical properties of red bricks in historical building in Rashid and overcome the ordinary materials.

Compressive strength for sample (J) after treatment with Nano Silica of 1.5% concentration and Nano Titanium of 1.5% concentration with (Waker Bs15) Bs15 materials of 20% concentration in water give the highest load of 28.49KN by an increase of 250% with respect to the control one which give a compressive strength of 113kg/cm².

Ultrasonic puls velocity for sample (J) after treatment with Nano Silica of 1.5% concentration and Nano Titanium of 1.5% concentration with (Waker Bs15) Bs15 materials with 20% concentration in water give the highest velocity of 2334 m/s with an increase of 48.56% of the control sample which give 1571m/s

Physical properties for sample (J) after treatment with Nano Silica of 1.5% concentration and Nano Titanium of 1.5% concentration with (Waker Bs15) Bs15 materials with 20% concentration in water give the highest bulk density of 1.64gm/cm³ with an increase of 31.2 % of the control sample which give 1.25gm/cm³.

References

- [1] H. Lloyd, **Collections Outdoors**, in the First Manual of Housekeeping Butter Worth the Heinmann, London, 2006, pp. 581.
- [2] V. Cnudde, G. Silversmit, M. Boone, J. Dewanckele, B. De Samber, T. Schoonjans, D. Van Loo, Y. De Witte, M. Elburg, L. Vincze, L. Van Hoorebeke, P. Jacobs, *Multi-disciplinary characterisation of a sandstone surface crust*, **Science of the Total Environment**, **407**(20), 2009, pp. 5417-5427.
- [3] S. Modestou, M. Theodoridou, I. Ioannou, *Micro-destructive Mapping of the Salt Crystallization Front in Limestone*, **Engineering Geology**, **193**, 2015, 337-347.
- [4] J.L. Hull, *Can Nanolimestone Consolidation Offer a Feasible Conservation Method for Limestone Ecclesiastical Buildings?* **Dissertation BSc** University of the West of England, Bristol, 2012, pp. 1- 47.
- [5] B. Ratoi, V. Pelin, I. Sandu, M. Branzila, I.G. Sandu, *Hidden Message in Stone Masonry of Galata Monastery - Iasi City, Romania*, **International Journal of Conservation Science**, **9**(1), 2018, pp. 151-164.
- [6] M. El-Gohary, A. Metawa, *Cleaning of architectural bricks using RF plasma. I. Metallic stains*, **International Journal of Conservation Science**, **7**(3), 2016, pp. 669-682.
- [7] H. Derluyn, J. Dewanckele, M.N. Boone, V. Cnudde, D. Derome, J. Carmeliet, *Crystallization of non ISIHdrated and Anhydrous Salts in Porous Limestone Resolved by Synchrotron X-ray Microtomography*, **Nuclear Instrument & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms**, **324**, 2014, pp. 102-112.
- [8] M. Steiger, A.E. Charola, K. Sterflinger, *Weathering and Deterioration, Stone in Architecture. Properties, Durability* (5th edition), (Editors: S. Siegesmund and R. Snethlage), Springer Verlag, Berlin, 2014, pp. 225-316.
- [9] R. Anu Padma, R. Ramasamy, M.S. Mathews, *Chemical weathering of a granite stone sample from the Peruvudaiyaar Koil, Thanjavur, Tamil Nadu, India*, **Journal of Applied, Geology and Geophysics**, **1**(2), 2013, pp. 39-53.
- [10] A. Moncrieff, G. Weaver, **Cleaning** (first edition), Crafts Council Conservation Science, London, 1983, p. 12.
- [11] S. Hemed, *Seismic Response Analysis and Protection of Underground Monument Structure the Catacombs of Kom El Shogafa Alexandria, Egypt*, **Advances in Geotechnical Earthquake. Soil Liquefaction and Seismic Safety of Dams and Monuments** - In Tech.Open, 2012, pp. 73-85.
- [12] H.S. Badawi, S.A. Mourad, *Observations from the 12-October-1992 Dahshour Earthquake in Egypt*, **Natural Hazards**, **10**(3), 1994, pp. 261-274.

- [13] S. Scheerer, O. Ortega-Morales, C. Gaylarde, *Chapter 5 Microbial Deterioration of Stone Monuments-An Updated Overview*, **Advances in Applied Microbiology**, **66**, 2009, Pages 97-139.
- [14] V. Korolev, *Implementation Principles of Nanotechnology in Constructional Material Science*, **5th International Conference on Nano-technology in Construction**, Housing and Building National Research Center, 2013, pp. 107.
- [15] M. Stefanidou, I. Papyianni, *The Role of Nano Particles to Water Repellency of Lime-Based Mortars*, **Conference Recent Progress in the Consolidation of Calcareous Materials**, 21-22 April, Litomyšl, Czech Republic, 2010, pp. 1 - 6.
- [16] P. Maravelak-Kalaitzaki, Z. Agioutantis, E. Lionakis, M Stavroulaki, V. Perdikatsis, *Physico-chemical and mechanical characterization of hydraulic mortars containing nanotitania for restoration applications*, **Cement and Concrete Composites**, **36**, 2013, pp. 33 - 41.
- [17] A.F. Gordina, Y.V. Polyanskikh, A.F. Tokarev, *Water Resistance Gypsum Materials Modified with Cement, Silica Fume and Nanostructures*, conference: **5th International Conference on Nano-Technology in Construction, House and Building National Research Center**, 2014, pp. 107.
- [18] L. Pinho, F. Elhaddad, D.D. Facio, M.J. Mosquera, *A novel TiO₂-SiO₂ Nanocomposite Converts a Very Friable Stone into a Self-Cleaning Building Material*, **Applied Surface Science**, **275**, 2012, pp. 389-396
- [19] M. Stella, M. Bellusci, F. Fernandez, F. Persia, *Testing of Nanostructured Products for Protection and Consolidation of Biocalcarenite*, **Proceedings of the Conference BUILT HERITAGE 2013 Monitoring Conservation and Management**, Milan, Italy, 18-20 November 2013, pp. 1454-1460,
- [20] M. Licchelli, M. Malagodi, M. Weththimuni, C. Zanchi, *Nano Particles for Conservation of Bio-calcarenite Stone*, **Applied Physics A-Materials Science and Processing**, **114**(3), 2014, 114, pp. 673-683.
- [21] I. Karapanagiotis, D. Grosu, D. Aslanidou, K. Aifantis, *Facile Method to Prepare Superhydrophobic and Water Repellent Cellulosic Paper*, **Journal of Nanomaterials**, **2015**, 2015, article number: 219013, DOI: 10.1155/2015/219013

Received: August 20, 2017

Accepted: November 18, 2018