

Physical and Mechanical Characteristics of Helwan Limestone: For Conservation Treatment of Ancient Egyptian Limestone Monuments

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Abstract: This paper describes the evaluation result carried out to ascertain the effectiveness of consolidation treatments applied on fresh specimens of Helwan protected Quarry, which extensively used in Ancient Egyptian monuments. The experimental were carried out using non-destructive methods for assessing the performance of Helwan limestone before and after treatments with four synthetic polymers which have been extensively used in stone conservation to preserve monuments from further deterioration. Physical and Mechanical properties of fresh limestone samples were determined in order to provide reliable data and significant guideline for the selection of suitable consolidant for conservation and maintenance process could be applied on Ancient Egyptian limestone monuments, statues, carved facades, decorative elements and historical structures. The selected stone substrates and, before treatment with the polymers, they were demonstrated formation of qualitative level-marking parameter according to the system of qualification. Selection of different non-destructive methods are applied and compared to understanding of material structure and physico-mechanical behavior, such as real and apparent density, bulk density (Kg/m³) of the fresh and treated samples. Measuring of US Time (μ s) and calculation of US velocities (Km/s) under laboratory conditions before and after the conserving trials. Duroscope rebound values before and after the conserving material, water absorption by capillary-rise and total immersion. The absorption rate of stone consolidant was also recorded. The textural properties of limestone samples were described by using petrographic microscope and X-Ray Diffraction (XRD).

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Key Word: Conservation; consolidation;. Helwan limestone. Egypt. Monument. Aliphatic uretan resin (Z.K.F). silica acid ester Wacker-OH.(PMMA: Polymethyl methacrylate).(B-72).Acrylate resin (ACR). non-destructive methods. Physical and Mechanical properties. Density. Duroscope rebound values .water absorption. Water capillary.

1. Introduction

Limestone materials are widely used as artwork and building materials in many areas around the World. Some of these monuments and artwork represent the most important culturally significant throughout the World (Fitzner, 2002, Papamichos, et al., 2006, Al-naddaf 2013). Limestones can exhibit considerable differences in their behavior on exposure, even within the same limestone succession (Aboushook, et al., 2006). The Egyptian limestone buildings, monuments, statues, carved facades and other structures are threatened by varying degrees of cosmetic damage, not only because of the years they are standing, but also due to the aggressive urban environment factors, and the ambient climatic conditions of the last decades, such as increase of the atmospheric pollution, fluctuations in

temperature and humidity, urbanization, people living nearby, industry, rising of water table and tourism. In addition of many clear different processes of weathering, there is a complex interaction of physical, chemical and biological processes that contribute to the deterioration of stone monuments, in some general or specific way.(Winkler, 1997, Papamichos et al., 2006, Nuhoglu et al., 2006, Pandey, 2013, Dalimi1, et al., 2013). Among the most serious aspects of a restoration project in case of stone monuments, the using of incompatible of the original building material with new material inserts used for the completion of damaged structural (Kourkoulis, 2006). Numerous mistakes in stone preservation in the past can be attributed to the lack of knowledge and experience of the natural stone substance and subsequent

restoration practice of Cultural significance (Exadaktylos, 1998, Sidraba, 2001) and using of inappropriate conservation treatments which cause serious and un re-medical damage of ours value monuments.

Helwan protected limestone quarry one which has been extensively quarried from pre-Dynastic times until Greco-Roman Period, Coptic, Islamic time, and into the present century. Used for building material, temples, sculptural, carved facades, decoration and other works of art (Bard, 2005, Klemm & Klemm, 2002, Fitzner, et al., 2002, Harrell & Storemyr, 2009) and still uses for stone replacement or rebuilding works at historical monuments of the entire region of the Giza plateau. Helwan limestone, easily quarried by wedging and cutting and the subsequent separation of blocks of suitable size. Helwan limestone is refer to Mokattam formation (meddle Eocene). All the present monument stones around Cairo are made of Eocene rocks from the ancient quarries (Siegesmund, 2002, Kammar, 2013). Eocene limestone outcrops within the boundaries of the Cairo area provided the material for the construction of most historical stone monuments, ornament facade and decorative elements in this region, building the pyramids, temples, castles, towers, mosques, monasteries and palaces since the Pharos time to the medieval ages. Sphinx, as well as other status, had also been sculptured in similar limestones. These were, in particular, Mokattam limestone plateau east of Cairo, Helwan limestone plateau in the southeast and the Giza limestone plateau in the western part of Cairo..(Aboushook, et al., 2006). The Eocene limestone is varies in texture and quality with bewildering variety.

The study of rocks is based on a science that uses many properties for identification and classification. Understanding these properties will not only help conservators understand the physical and mechanical properties of materials they are using, but will help them in the decision making of the optimum restoration and preservation as the selection of compatible consolidant materials and methods, and to assess the effectiveness and

suitability of treatment methods. In the other hand, determining the mechanical properties of stones is vital to study the decay process and measure the degree of damage of monumental stones, to evaluate their conservation state and to assess the conservation action that must be applied (Exadaktylos et al., 2000, Papamichos et al., 2006, Al-naddaf, 2013).

The importance and difficulty of selecting the most suitable type of natural stone in the case of replacement of damaged stone monument (Přikryl, 2007) and the most compatible consolidant, are often underestimated when planning and undertaking monument repair/restoration, even though is clearly understood by some conservator and architects. It is becomes necessary to any restoration operation, will planning and undertaking monuments and artworks restoration must be preceded by an exhaustive study of selected historical project, as mineralogical analysis and characteristics related to colour, texture and workability and physical properties such as apparent and absolute density, porosity, swelling (Kourkoulis, 2006) water evaporation and vapor permeability, salt attack. These study should be before and after treatment or replacement of damaged historical monuments, to know the improvement of (mechanical properties, durability, appearance, texture, etc.) and the decay period of the treatment itself (Fratini et al., 2006) as to evaluate the consolidant which will be apply, to prevent or reduce as much as possible stone deterioration.

Aim of the Research

Assessment of Helwan limestone as fresh material, commented in detail on the physical and mechanical properties, to assessing the performance of consolidated limestone before and after treatments with common commercial protective products Silica-acid-aester (Wacker-OH), Aliphatic uretan resin (Z.K.F), Acrylate resin (ACR) and Paraloid-72 (B72) in order to provide reliable data and significant guideline for the selection of

suitable methods for conservation and maintenance could be applied on Ancient Egyptian limestone monuments, statues, carved facades and other structures

2. Methodology

The experimental were carried out using practical non-destructive methods for assessing the performance of surface before and after treatments with four synthetic polymers which have been extensively used in stone conservation to preserve monuments from further deterioration. The products, which have been applied, are selected according to their frequent use in the field of stone conservation. [Table 1] shows the most important parameters of fresh Helwan protected limestone and applied stone consolidants.

The laboratory experiments were done with cubic specimens of (5 cm) to determine the structure properties and evaluation of consolidant treatments applied. From fresh blocks of Helwan Quarry, (Cairo - Egypt) more than 75 specimens were cut in cubic of (5 cm) by using diamond saw [Figure 1], the selected stone substrates and, before treatment with the polymers, they were demonstrated formation of qualitative level-marking parameter according to the system of qualification [Table 6]. The physical parameters of each test specimen were analysed before the treatment included measuring the cubs and weight of all specimens. Comparable physical properties such as real density of fine powder by Pycnometer, performing density determination using the Pycnometer method (in Accordance with German and European Standard DIN EN

725-7) and apparent density, bulk density (Kg/m³) of the fresh and treated samples, apparent porosity was determined according to the test procedures described in the European standard EN 1936. Measuring of US Time (μ s) and calculation of US velocities (Km/s) (Controls Ultrasonic tester E-46) were determined under laboratory conditions before and after the conserving trials. For each test specimen five measurements were made and average values and standard deviations were calculated. The textural properties of limestones were described by using petrographic microscope. Mineralogical composition was determined by X-Ray Diffraction (XRD) with a Phillips Diffractometer (PW 1130 generator, PW 1050 goniometer, Cu anode and monochromator, 40kV, 20mA, angle 5°-70°, step size 0.02°, time per step 1.0 second). Characterizing the different types of moisture transport involved, water absorption by capillarity rise method on Rectangular prism of (5cm) square and on 40 cm-long blocks (procedure is described in the European standard EN 1925). This method is aimed to evaluate the kinetics of water absorption and to provide an estimation of the penetration depth of consolidants into the porous stone. Water saturation by total immersion of cubic specimens were measured, The absorption rate of stone consolidant was also recorded on test cubes. The post-conservation tests were performed on fully saturated cubic samples 5 months after the first treatment trials. Duroscope rebound values were determined under laboratory conditions before and after the conserving material.

Table 1. Stone Consolidants and their Properties (AHMED, 2004)

| Consolidation | Diluting Agent | Density [g/cm ³] | Viscosity [mPas] |
|--------------------------------|------------------------|------------------------------|------------------|
| Silica-acid-aester (Wacker-OH) | Ready to use | 0.9793 | 2.8 |
| Paraloid-72 (B72) | Nitro-thinner | 0.8460 | 9.3 |
| Aliphatic-uretan-resin (Z.K.F) | White spirit "aromatic | 6.5 | 2.5 |
| Acrylate resin (ACR) | White spirit | 0.7788 | 6.5 |

3. Materials

3.1. Provenance of limestone

Egyptian limestone towards the north, up to Helwan is consisting predominately of calcite (calcium carbonate, CaCO_3) and concentrated on the vary from marly, dense rocks and highly resistant, contains fossil (Molluscs, and especially echinoids and Globigerinid, Nummulitid foraminifera, Ostreaelegans, Pecten, *Lucina mokattamensis*) plus one or more of the following impurities: dolomite (calcium magnesium carbonate, $\text{CaMg}[\text{CO}_3]_2$); quartz (silica, SiO_2 , as detrital sand silt grains or diagenetic chert nodules); iron oxides (haematite, FeO_3 , or goethite, HFeO_2) and various clay minerals (aluminosilicates) (Nicholson & Shaw, 2000, El-Adawy, 2008). The character and qualities of various Egyptian limestones have been considered by several authors in the context of their economic utilization, especially as building stones (Bradley, 1989, Klemm & Klemm, 2002, Young, et al., 2009).

Limestone was perhaps the first rock used for building purposes in Ancient Egypt. Limestone was also used for tomb superstructures in the north, and for blocks carved in relief on the walls of rooms, temples built of fine limestone, especially in the Delta (Bard, 2007). The earliest examples are a possibly late predynastic tomb at Qau el-Kebir and some first Dynasty tombs at Abydos and Memphite region. First Dynasty tombs of courtiers, particularly at Abydos, were often marked by a limestone stela with the name, and sometimes the titles, of the deceased [Figure 2]. Helwan plateau (Eastern river side of the Nile and Giza plateau (few km west from the Nile) (Ahmed, 2006). The old Helwan limestone quarry is about 35 kilometers south of Cairo (Khaled, 2008). Helwan is modern name for the important Early Dynastic cemetery on the east bank of the Nile ($29^\circ 51' \text{ N}$, $31^\circ 22' \text{ E}$), opposite Saqqara and 21km south of Cairo (Bierbrier, 2008). The Early Dynastic tombs were furnished with a wide variety of grave goods. Some of the (1st–2nd Dynasties) tombs at Helwan show extensive use of limestone for

portcullis blocks, flooring, wall-lining in burial chamber and roofing (Nicholson, 2000, Bard, 2005). The entire region of the Gizeh plateau up to the escarpments of Sakkara and Mokattam-Tura- Ma'sara, Helwan plateau, belongs stratigraphically to the Mokattam Group, which is subdivided into quite a number of diverse members and facies, all of them belonging to the upper Lutetian. The Mokattam Group in its south and southeastern part at Helwan area interfingers with Helwan facies of Middle Eocene. It consists of about 77m of white to yellowish white, marly and chalky limestone intercalated with hard, grey dolomitic limestone bands. The rock is relatively soft and easy to work with due to the abundant calcite (calcium carbonate, CaCO_3). These fine limestones were also mined for many different purposes during the entire Egyptian history, until today, when they mainly supply the extensive lime and cement industries of Tura and Helwan (Klemm & Klemm, 2002, El-Adawy, 2008). The extensive deposits of Mokattam, Tura-Ma'sara, and Helwan limestones contain thinly bedded intercalations of more or less marly limestone with a small amount of clay. The colour varies according to the composition. Generally speaking, limestone is typically light to moderate grey in colour when fresh, but does exhibit a wide range of shades from nearly white or cream to yellowish white and whitish yellow to yellowish, and grey. The stone extraction of Helwan plateau, mainly used for building, temples, stelae, statues, other sculptures and others decorative details. Investigation into the decay of Helwan limestone noted the importance of soluble salts, whether inherent in the rock as quarried or drawn into the stone by capillary action from surrounding groundwater [Figure 3]. evaluation of weathering forms and monument mapping made from limestone in the center of Cairo show a clear correlation between the damage and salt loading of the limestone as a consequence of air pollution and rising humidity (Siegesmund, 2002, Aboushok & Park, 2006).



Figure 1. Fresh Helwan Limestone specimens



Figure 2. 1st - Dynasty limestone stela of King Djed, The earliest convention of writing the royal name is in the format of the serekh rectangular design surmounted by the Horus falcon, from his tomb at Abydos.

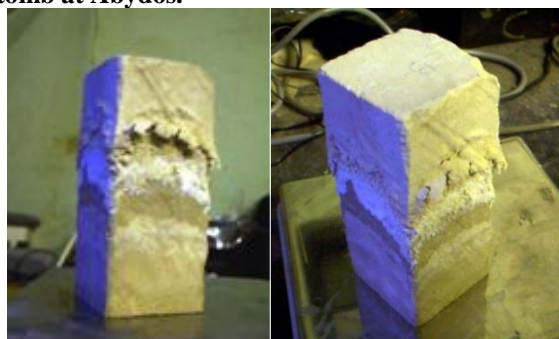


Figure 3. Salts crystallization on the surface of the rocks by capillary action.

3.2. Texture and mineralogy

Helwan limestone is very fine-grained. X-Ray powder diffraction (XRD) analyses of Helwan limestone samples were carried out. XRD traces of samples were obtained at the Geological Engineering Department in Budapest. The major advantage of X Ray

diffraction techniques, obtaining structure of substance thereby allowing identification of a mineral, or calculation of structure of a compound. According to XRD analyses Helwan Limestones composed chiefly of calcite limestone (CaCO_3) mineral and a smaller proportion of other minerals, including various clay minerals such as Montmorillonite, Halloysite, (aluminosilicates), Vermiculite, As well as consists gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and Tridymite, Boehmite [Plate 1]. Gypsum formation strongly depends on the mineralogical composition and the rock fabric [Figure 3]. Helwan limestone has a white creamy colour. Under the microscope with different magnification [Plate 2] is formed mainly of fine-textured amorphous lime with silty/sandy (quartzose) and with the interspaces filled with fine-textured crystalline mosaic calcite. There are few small detrital quartz and the limestone samples contains of foraminifers, plecypod fragments, echinoderms and other shell fragments and one of the forms of codiacean alga, Halimeda.

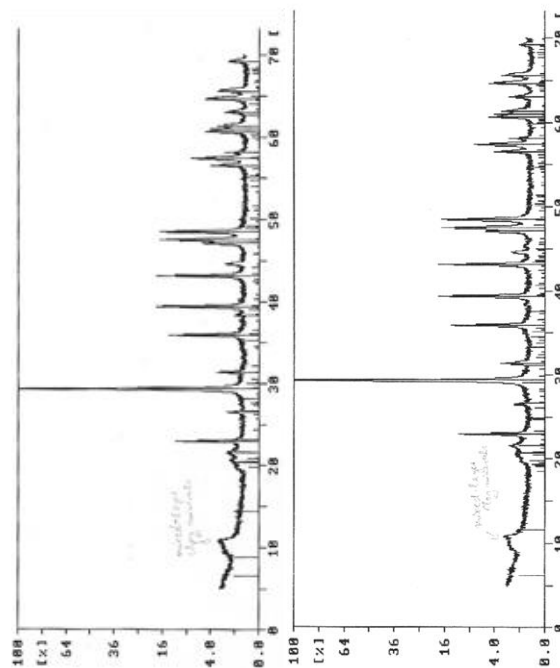


Plate 1. X Ray Diffraction of fresh Mokattam limestone samples shows that Calcite (CaCO_3) is a main mineral and consistence of Ca Mg (CO_3) and some clay minerals

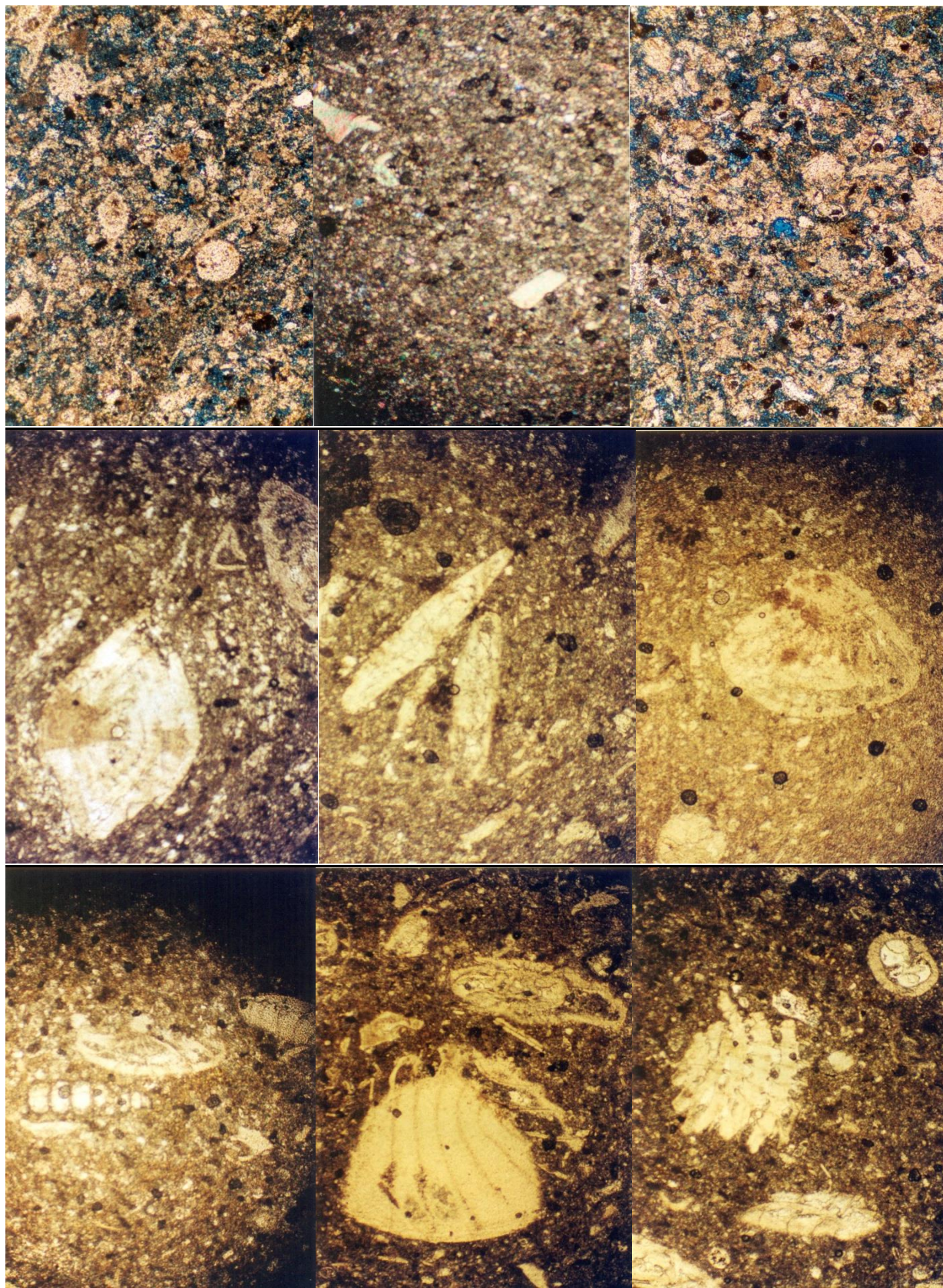


Plate 2. Thin section photograph of fine grain Helwan Protected limestone with different magnification.

3.3. Physical and Mechanical Properties

To reconstruct and preserve the stone monuments it is necessary to measure and rely on the physical and mechanical properties to evaluate the degree of damage induced by weathering before any applying of treatments. Mechanical properties reflect the effect of the consolidation treatment to the internal cohesion of the stone matrix, and the adhesion between stone constituents (Karatasios, et al., 2009). Further, the Building Stone Preservation and Restoration of Historical Monuments sectors are seeking for guidance for effective test standards (laboratory and in situ) to measure accurately Natural Building Stones (NBS) strength and deformation characteristics. The structure properties that are fundamental in describing porous materials are porosity, pore size distribution, pore shape and specific surface, water absorption, permeability. comparable physical properties for bulk density and real density.

3.3.1. Density

Density is one of the most fundamental properties of geological materials. Minerals on Earth have a rather limited range, from about 2.0 g/cc for some zeolites (~0.9 for ice) to 7.6 g/cc for galena (22.6 for native iridium). Rocks, which are masses of various minerals, have an even more restricted range of density. The density (ρ) is the proportion of mass (m) of material to volume in an amount of material (VO). For a homogeneous object it is defined as the ratio of its mass (m) to its volume (V) follows equation.

$$\rho = \frac{m_i}{v_o}$$

The test methods which are carried out to determinate density are: -

1- Determining the “apparent density” regular-shaped objects. The equation were used to calculate the bulk density parameter were:

$$\rho = \frac{m_i}{v_o} \times 10^3$$

2- Part 2: Determining the real density of fine powder by Pycnometer [Table 2]. The

fluid used for an Egyptian Helwan sample was absolute alcohol because the limestone samples contains salt. The stone samples were fresh limestone crushed in a very fine powder to measure the real density. The equations were used to calculate the density of powder is:

$$m_p = (m_2 - m_1)$$

$$V_f = \frac{(m_3 - m_2)}{\rho_{f1}}$$

$$V_{picno} = \frac{(m_4 - m_1)}{\rho_{f1}}$$

$$V_o = V_{picno} - V_f$$

$$\delta\rho = \frac{m}{v_o}$$

3.3.2. Bulk Density, factor variation and ultrasonic sound velocity

Bulk densities are important in quantitative soil studies, and measurement should be encouraged [Figure 4]. The determination usually consists of drying and weighing a per unit volume of the rock sample. The important result which we can get from bulk density measurement, that the greater the density, the less pore space for water movement [Table 6]. The equations were used to calculate the bulk density porosity are:

$$BulkDensity = \frac{Weight}{Volume}$$

$$Porosity\% = 1 - \left(\frac{BulkDensity}{ParticleDensity} \right) \times 100$$

The factor variation is an important parameter to sort samples according to physical quality of rock. As it follows from equation

$$Mi = \frac{1}{\delta_e} (p_{oi} - p_o) + \frac{1}{\delta_c} (c_{oi} - c_o)$$

The equation were used to calculate the ultrasonic sound velocity parameter were:

$$c_o = \frac{S_i}{t_{oi}}$$

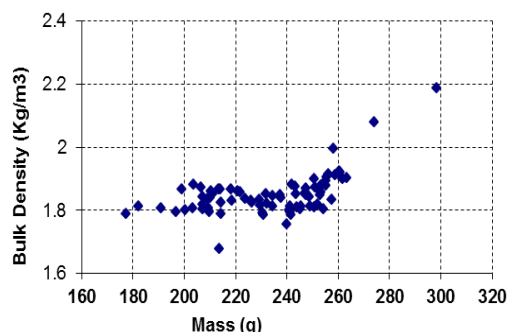


Figure 4. the Bulk Density of drying (Helowan Protected Quarry) Limestone before treatment

3.3.3. Water absorption coefficient

Absorption is the process by which water is absorbed. The Absorbency measurement of water is an important laboratory test to determining the characterization factors of porous stone materials. Absorbency is the result of two properties, porosity and permeability. Porosity and permeability are probably the most important physical properties of rock study of decay and corrosion of building and stone monuments (Robertson, 1982). The water absorption coefficient and transport velocity under specific conditions depends on the amount of water offered, moisture content, distribution and pore structure, density, the size of the pores, their orientation, how well they are networked and the type of finish the stone has, are important contributing factors to a stone's overall absorbency et al., 2009, Binder, et al., 2010). The water absorption coefficient describes the rate and the maximum water absorption capacity of stone. These effects are caused by the porous structure of stone and the reactivity of its chemical components. The amount of water absorption usually expressed as percentage of the dry weight of the material. The important aspects of modelling the water absorption kinetics could help conservators in water absorption simulation for predicting the suitable absorption conditions.

In addition water permeability of a material is affected when its surface is obscured by the presence of atmospheric soiling or biological growth, or, when there are hygroscopic salts within the interior (Ahmed, 2004). The

formation of a weathering crust due to mineralogical changes occurring on the exposed (weathered) surface may substantially affect water permeability measurements (Winkler, 1973, Přikryl, 2007). By comparing data obtained on masonry that has been exposed to the elements with measurements made on un-weathered samples, it is possible to measure the degree of weathering that has occurred. Therefore the test Method provides useful information when carried out even on un-weathered samples. As the test method can be used to evaluate the performance of a water consolidants treatment. An effective treatment should substantially reduce surficial permeability of the stone material to water.

3.3.3.1. Water Absorption Coefficient by Capillary

The measurement of capillary water absorption is a convenient way to evaluate the kinetics of water absorption, the amount of water absorbed by means of capillary rising damp process and to estimating the penetration depth of consolidants material into the porous

The test has been done in the laboratory condition at a temperature of 20 ± 2 on Rectangular prism of (5cm) square and on 30 cm-long blocks, follow the proceeding and formula to evaluate how is networked are absorbing. Prior to the performance of the absorption tests, all the samples were dried until constant mass was recorded. Respectively, data of the water level and weight increases recorded began after 30 second multiplied [Figure 5]. The samples were standing in de-ionized water in constant water level to a depth of (4 ± 1) mm [Figure 6].

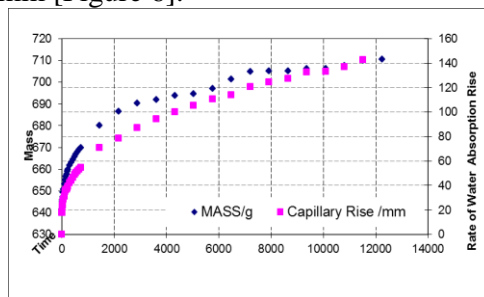


Figure 5 Water Absorption By Capillary Rise - Egypt Helwan Protected Quarry



Figure 1. The immersed specimens in constant water level

3.3.3.2. Water Absorption Coefficient by Total Immersion

The test has don follow the proceeding and formula of untreated samples [Figure 7] to evaluate how is networked are absorbing after the treatment and how the treatment effective substantially reduce surficial permeability of the material to water. This test measures the coefficient of water absorption rate and the maximum water absorption capacity. The total quantity of water absorbed is related to the total open porosity. The specimens were dried Prior to the performance of the absorption tests to constant mass at a temperature of 70 ± 5 oC and weighed (md). The specimens were totally immersed in the deionized water. Respectively data of water absorption incensement recorded began after 30 second multiplied. All the tests were finished when saturation was attained for a period of 48 hours [Table 3]. A graph, representing the mass of water absorbed of the untreated immersed specimens compered with consolidated cubic specimens by different consolidant as a function of time was plotted [Figure 8]. The water absorption capacity (WAC) was calculated using the follow formula:

$$WAC = \frac{m_{\max} - m_d}{m_d} \times 100$$

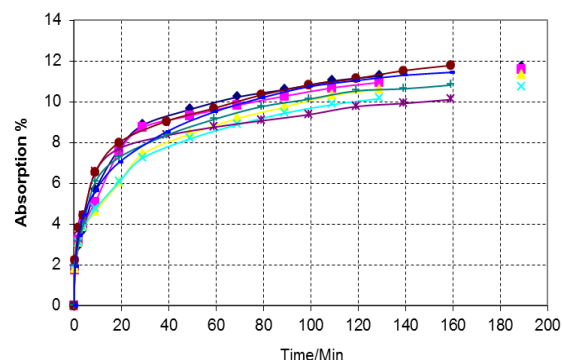


Figure 7. Water saturation of fresh Helwan protected quarry

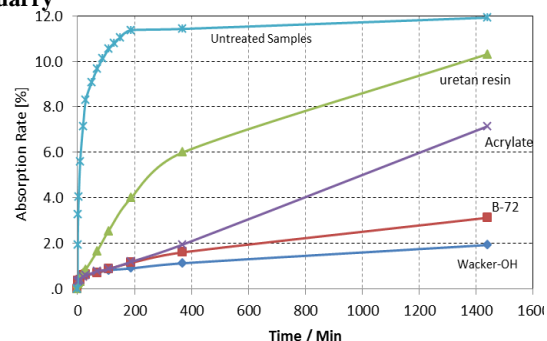


Figure 8. Water absorption after secon cycles of consolidation compared with untreated samples

4. Consolidation Tests

4.1. Absorption rate

According to accelerating deterioration of exposed historical buildings, sculptures, decorative surfaces of architectural monuments and others stone ornament, consolidation is considered to be one of the major conservation interventions in an attempt to preserve the external weathered layers of historical monuments and reduce their degradation rate (Karatasios et al., 2009). The main function of stone consolidants is to reestablish the cohesion between particles of deteriorated stone. In addition, a good consolidant should meet performance requirements concerning durability, depth of penetration, effect on stone porosity, moisture transfer, compatibility with stone, and on appearance (Clifton, 1980). These performance considerations to become the basis for stone consolidant specifications.

The efficiency of consolidant treatments was assessed by comparison of different physical properties in laboratory condition. These laboratory studies have demonstrated that the

absorption rate of various consolidation of stone samples for first and second cycles, compared to water absorption of non-treated samples at room temperature. [Figure 9, 10] show the absorption rate of various consolidants in Helwan limestones compared to water absorption of non-treated samples at lab temperature. The average penetration of first cycle varies between 10.16% of Polymethyl methacrylate (B-72) to 13.75% for Wacker-OH after 24 hours of saturation [Table 4]. The graphs [Figure 9] also illustrate that in general Wacker –OH and Uretan resin have a higher penetration rate than untreated samples. [Table 5] show the reducing of absorption average for second cycle between 5.59 % of Polymethyl methacrylate (B-72) to Aliphatic-uretan-resin (Z.K.F) 10.74 % after 24 hours of saturation and [Figure 10] also illustrate that in general most consolidants have a less penetration rate through first 2 hours of saturation, than first cycle.

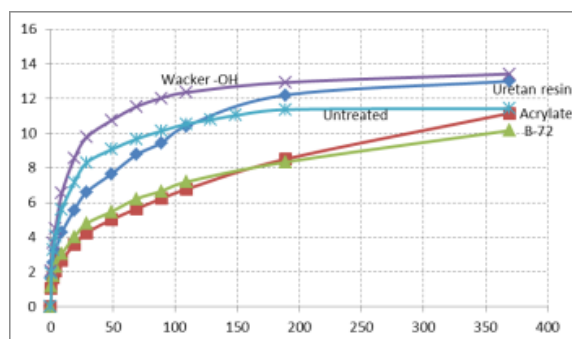


Figure 9. The first cycle of saturation with consolidants compared with untreated samples

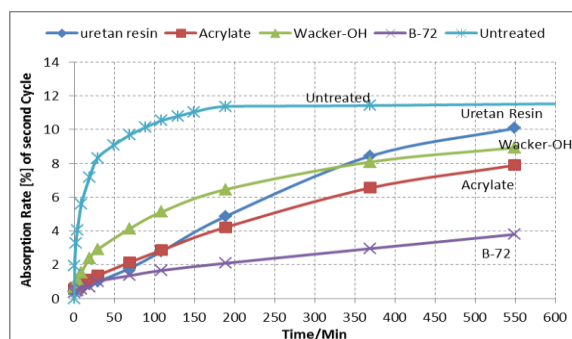


Figure 10. Average of different Consolidants Saturation in treatment for second time compared with untreated samples which saturated with water

5.2 Changes in Physical Properties

The petrophysical parameters show the increase of density after consolidation compared with untreated limestone from 0.5% to 1.081% and the maximum increase reached 5.61 % after the second cycle of consolidation by Wacker-OH. Ultrasonic sound velocities reflect improvement effect of various consolidants after first cycle. All values show a distinct increase after the treatment, but the most dramatic difference in velocities of untreated and treated samples was recorded after second cycle on silica acid ester Wacker-OH and Aliphatic uretan resin [Table 6].

Duroscope rebound value (surface strength) of consolidated Helwan limestone specimens compared to the non-consolidated samples shows an average strength increment of treated samples [Table 6]. the percentage increase of strength was with Aliphatic uretan resin (Z.K.F) 23.30 % [Figure 11], whilst with Wacker-OH 48.15% [Figure 12] shows the most dramatic increase in surface strength, followed Polymethyl methacrylate (B-72) 39.84 [Figure 13], whereas with Acrylate shows the less increase with the Surface strength 16.29 % [Figure 14]

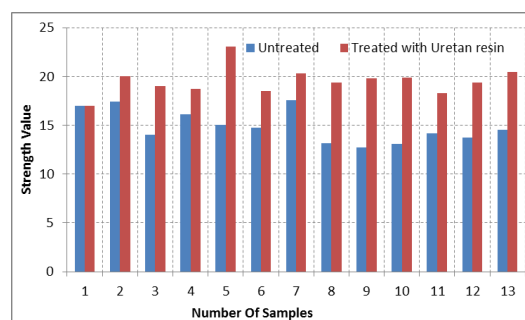


Figure 11. Duroscope rebound before and after treatment with Aliphatic-uretan-resin (Z.K.F)

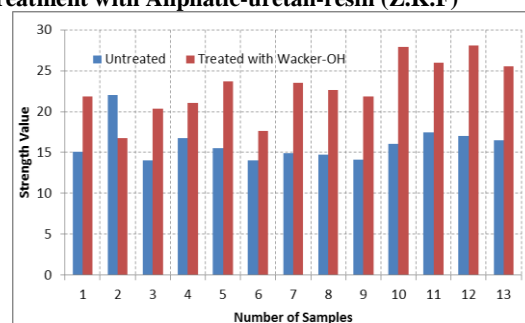


Figure 12. Duroscope rebound before and after treatment with silica acid ester Wacker-OH

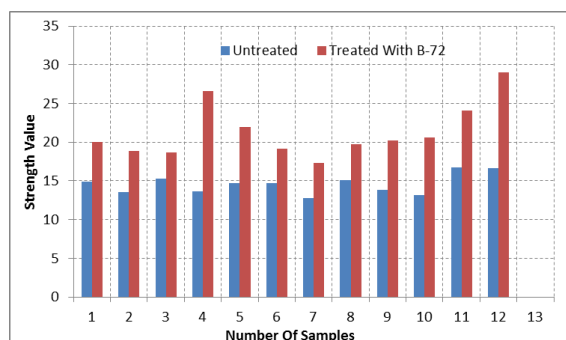


Figure 13. Duroscope rebound before and after treatment with (PMMA: Polymethyl methacrylate)

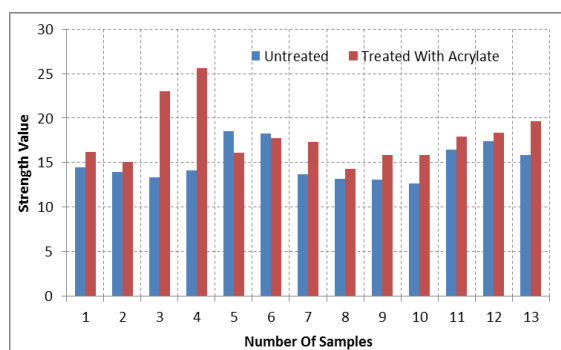


Figure 14. Duroscope rebound before and after treatment with Acrylate resin (ACR)

5. Result and Discussions

A significant Number of the built heritage Monument in Cairo-Egypt is made of limestone which belong to Mokattam formation. A huge number of our built heritage in Egypt and around the World heritage belongs to limestone. Therefore a knowledge about characteristics and classification of Helwan limestone, would be valuable to the conservation of stone art work and architects. It would help him in choosing correct raw and consolidant material, as well as conservation techniques in conservation and restoration works which will prevent or slow the rate of decay in the historic monuments.

The texture and mineralogy of Helwan limestones contains various of swelling clay minerals and Ca-sulphates (gypsum and bassanite) [Plate 1]. The laboratory tests of non-treated cubic test specimens also have proven that the average of real density 2.87 with standard deviation 0.12 and average apparent density as the average of open pore

water saturation 12.06 whereas the porosity 35.59 [Table 2]. Bulk density is a measurement of the weight of the rock samples for a given volume. Variation in bulk density is attributable to the relative proportion and specific gravity of solid organic and inorganic particles and to the porosity of the rock. The average of bulk density (kg/m³) before treatment for Helwan limestone 1.85 (kg/m³) with standard deviation (STD) 0.07 [Table 6].

The result of Duroscope rebound value test as (Nun-Distractive) method to estimate the surface strength shows the average value of Helwan untreated limestone has value 15.41 [Figure 15]. According to Duroscope rebound test the limestone strength value has a positive effect of consolidation on the mechanical properties of the natural stone is observed after application of various consolidants, which varies according to the product [Figure 11, 12, 13, 14]. Where strength of specimens, attributing to silica acid ester Wacker-OH were able to penetrate limestone specimens in considerably higher, reaching 48.15% an increase of strength values and 39.84% with (PMMA: Polymethyl methacrylate) followed 23.30% with Aliphatic uretan resin (Z.K.F) and 16.29% with Acrylate resin (ACR).

Ultrasonic velocity test shows average of longitudinal waves before treatments for - Tura samples is 2.55 (Km/s) with standard deviation (STD) 0.17. The longitudinal waves of ultrasonic velocity became longer specially after second cycle of treatments with all stone consolidants [Table 6] with various longitudinal waves from one agent to the second. Ultrasonic velocity measurements (P- and S-waves) are applied to determine the quality of Helwan limestone samples in order to demonstrate its homogeneity or its degree of alteration. (PMMA: Polymethyl methacrylate) consolidant has the highest incensement of longitudinal wave comparing with the others agent. Followed silica acid ester Wacker-OH and Aliphatic uretan resin (Z.K.F). Acrylate has the less longitudinal wave after first and second saturation cycle among whole consolidant types. This is

mainly may due to the limited absorption of acrylic consolidant and the formation of a very thin surface layer. After second saturation cycle Aliphatic uretan resin (Z.K.F) become the first in longer longitudinal waves followed silica acid ester Wacker-OH and (PMMA: Polymethyl methacrylate). Bouineau (1978) proved the relation between ultrasonic velocity, compressive strength, modulus of elasticity and apparent density of the material (Bourgès, 2006).

In relation to the results of the test measurements are presented in the form of a water absorption graph with the volume of water absorbed in cubic centimeters reported as a function of time in minutes [Figure 6]. As the absorption profiles obtained in the whole specimen tests of untreated Helwan limestone show an initial phase with a high absorption rate 3.28% during the first 2 minute compering with consolidated samples. The samples treated with silica acid ester Wacker-OH after 24 hours are the less in water penetration 1.93% followed (PMMA: Polymethyl methacrylate) 3.13% whereas Aliphatic uretan resin show dramatic penetration 10.31% compared with untreated samples 11.91% [Table 3]. In contrast to the rate of Water absorption of treated samples, the absorption rate of fresh specimens by Wacker-OH in first cycle becomes of particular interest for the first 2 minutes 3.70% comparing with water absorption of untreated samples with 3.24%. Considering consolidant absorption rate, after 24 hours of, Wacker-OH and Aliphatic uretan resin exceed the rate of water penetration in fresh specimens [Table 4]. The maximum absorption consolidant rate after 24 hours of second cycle for Helwan limestone specimens was with Aliphatic uretan resin 10.74 followed Wacker-OH and Acrylate whereas Polymethyl methacrylate reached 5.59% [Table 5].

In relation to the results, capillary absorption rates were expressed in %water absorbed/min, as the capillary absorption rate was defined also as the flux to a surface. Therefore, it was expressed as g/(cm²·min). The movement of a

liquid in the interstices of a porous material, as a result of surface tension, the phenomenon responsible for dry materials sucking moisture above the normal water level. We observed a close correlation between absorption levels with increasing weight [Figure 5] the coincidence of water levels is nearly the same as the weight of the sample because the amount of rise is inversely proportional to the pore and micro pore radius. This is the extent to which the pores and capillary structures are interconnected throughout the stone. These networks, their size, structure and orientation have an affect on the degree and depth to which moisture, vapors and liquids can be absorb into the interior of the stone or migrate from the substrate by capillary action through the stone. Permeability may be greater in some directions than others based on the pore size, shape and distribution of the system.

The open question why the Aliphatic uretan resin (Z.K.F) which water penetrated on limestone specimens up rate 10.31% compared with the silica acid ester Wacker-OH which has water absorption rate 1.93% are longer longitudinal waves after second consolidant cycle. It is suggested that the (Z.K.F) consolidant doesn't seal the open porosity and enhance cohesion of stone and consequently its durability, but not un-water repellent. Surprisingly why The mechanical strength of (Z.K.F) less than Wacker-OH and Polymethyl methacrylate. [Figure 8 and Table 3] presented the rate and speed of water absorption of consolidated specimens, Wacker-OH, Polymethyl methacrylate and Acrylate (ACR) are quiet similar of water absorption rate through the first 69 Minutes. whereas Aliphatic uretan resin (Z.K.F) have very high water absorption rate. [Table 6] shows the lees in increasing weight after draying of first cycle, Aliphatic uretan resin (Z.K.F) 1.65% whereas Wacker-OH 5.67% and after the second consolidant cycle, (Z.K.F) become 0.91% and Wacker-OH 2.23% whereas Acrylate resin 0.16% and B-72 0.24% weight increase

Table 2: Average values of physical properties - Helwan limestone untreated specimens

| Limestone Types | Average real Density | STD | Weight (g) of cubic 5 cm | STD of weight | Average apparent Density | Average of Open Pore by water Saturation after 24h | Porosity |
|-------------------------|----------------------|------|--------------------------|---------------|--------------------------|--|----------|
| Helwan Protected Quarry | 2.87 | 0.12 | 232.79 | 17 | 1.84 | 12.06 | 35.89 |

Table 3 Average of Water saturation of un-treated and treated cubic specimens with different consolidants

| Limestone Types | Time/min t ₀ | W-OH (%) | B-72 (%) | Z.K.F (%) | ACR (%) | Nun-Treated |
|-------------------------|-------------------------|----------|----------|-----------|---------|-------------|
| Helwan Protected Quarry | 2 | 0.35 | 0.35 | 0.27 | 0.32 | 3.28 |
| | 19 | 0.54 | 0.6 | 0.72 | 0.54 | 7.15 |
| | 69 | 0.71 | 0.72 | 1.67 | 0.78 | 9.4 |
| | 189 | 0.91 | 1.15 | 4.01 | 1.2 | 11.37 |
| | 1440 | 1.93 | 3.13 | 10.31 | 7.14 | 11.91 |
| | 2880 | 2.9 | 4.38 | 11.23 | 10.59 | 12.07 |

Table 4: Average after first cycle with different consolidants saturation and un-treated cubic specimens.

| Limestone Types | Time/min t ₀ | W-OH (%) | B-72 (%) | Z.K.F (%) | ACR (%) | Nun-Treated |
|-------------------------|-------------------------|----------|----------|-----------|---------|-------------|
| Helwan Protected Quarry | 0.5 | 2.06 | 1.19 | 1.63 | 1.05 | 1.94 |
| | 2 | 3.70 | 1.80 | 2.55 | 1.67 | 3.28 |
| | 19 | 8.55 | 4.02 | 5.57 | 3.60 | 7.15 |
| | 69 | 11.54 | 6.22 | 8.77 | 5.65 | 9.4 |
| | 189 | 12.93 | 8.34 | 12.21 | 8.51 | 11.37 |
| | 369 | 13.42 | 10.16 | 13.01 | 11.16 | 11.42 |
| | 1440 | 13.42 | 10.16 | 13.01 | 11.16 | 11.91 |

Table 5: Average after second cycle with different consolidants saturation and un-treated cubic specimens.

| Limestone Types | Time/min t ₀ | W-OH (%) | B-72 (%) | Z.K.F (%) | ACR (%) | Nun-Treated |
|-------------------------|-------------------------|----------|----------|-----------|---------|-------------|
| Helwan Protected Quarry | 0.5 | 0.68541 | 0.34388 | 0.41803 | 0.57481 | 1.94 |
| | 2 | 0.84416 | 0.42303 | 0.49303 | 0.63751 | 3.28 |
| | 19 | 2.38165 | 0.68591 | 0.85067 | 1.14547 | 7.15 |
| | 69 | 4.1281 | 1.3557 | 1.79121 | 2.13791 | 9.4 |
| | 189 | 6.45829 | 2.0918 | 4.87064 | 4.22467 | 11.37 |
| | 369 | 8.08478 | 2.95766 | 8.43463 | 6.54976 | 11.42 |
| | 1440 | 9.39558 | 5.58659 | 10.736 | 9.22582 | 11.91 |

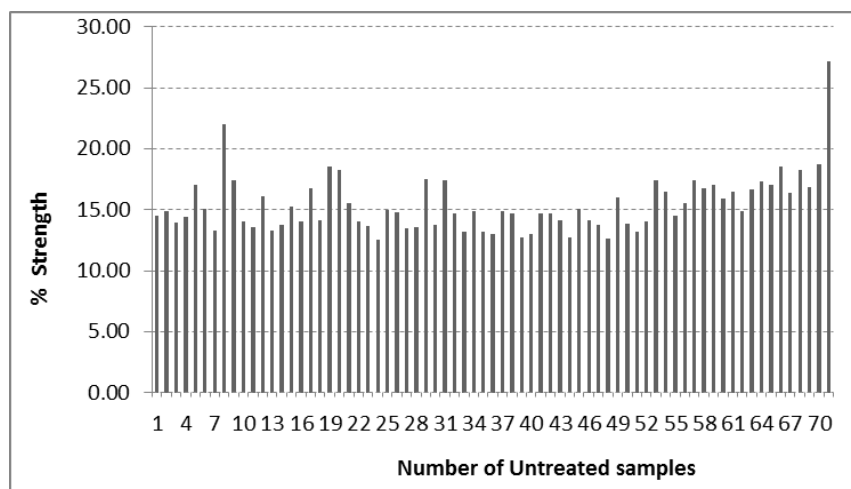
**Figure 15. Durosoprobe rebound of fresh Helwan protected quarry**

Table 6: An average of the physical property descriptions of Egypt Helowan limestone before and after the 1st and 2nd cycles of treatments

or treatments

| Before Treatment | | | | | | |
|--|---------------------|---------|-------------|--------------|---------------------|-------------------|
| Bulk Density | STD of Bulk Density | US Time | US Velocity | STD of USV | Strength | |
| Kg/m3 | Kg/m3 | | Km/s | Km/s | Duroscope Rebound | |
| 1.85 | 0.07 | 19.75 | 2.55 | 0.17 | 15.41 | |
| 1.84 | 0.02 | 19.4 | 2.57 | 0.13 | 14.86 | |
| 1.85 | 0.07 | 19.75 | 2.55 | 0.17 | 15.41 | |
| 1.83 | 0.08 | 19.8 | 2.54 | 0.11 | 16.01 | |
| 1.85 | 0.16 | 19.75 | 2.55 | 0.17 | 15.41 | |
| 1.85 | 0.12 | 19.7 | 2.56 | 0.08 | 15.01 | |
| 1.85 | 0.07 | 19.75 | 2.55 | 0.17 | 15.41 | |
| 1.84 | 0.08 | 19.7 | 2.56 | 0.15 | 14.58 | |
| | | | | | | |
| Average of First Cycle of Consolidant | | | | | | |
| Consolidants Absorption | 1 Month After dry | US Time | US Velocity | Bulk Density | STD of Bulk Density | Strength |
| (%) | (%) | | Km/s | Kg/m3 | Kg/m3 | Duroscope Rebound |
| Z.KF 12.46 | 1.65 | 19.00 | 2.62 | 1.87 | 0.03 | 19.52 |
| W-OH 13.75 | 5.67 | 19.00 | 2.65 | 1.94 | 0.09 | 22.83 |
| ACR 10.90 | 1.87 | 20 | 2.53 | 1.84 | 0.18 | 17.92 |
| B-72 12.03 | 1.68 | 18.7 | 2.69 | 1.87 | 0.08 | 21.55 |
| | | | | | | |
| Average of Second Cycle of Consolidant | | | | | | |
| Consolidants Absorption | 2Month After Dry | US Time | US Velocity | Bulk Density | STD of Bulk Density | |
| (%) | (%) | | Km/s | Kg/m3 | Kg/m3 | Kg/m3 |
| Z.KF 11.10 | 0.91 | 17.95 | 2.77 | 1.89 | | 0.03 |
| W-OH 9.68 | 2.23 | 18.37 | 2.76 | 1.96 | | 0.08 |
| ACR 8.64 | 0.16 | 19.45 | 2.61 | 1.83 | | 0.18 |
| B-72 7.15 | 0.24 | 22.80 | 2.68 | 1.88 | | 0.08 |

6. Conclusions

In general consolidation has a positive effect on the mechanical properties of the natural stone which varies according to the product. The mechanical strength results by Duroscope rebound values (surface strength) with all consolidants increased strength of the limestone surface. Silica acid ester Wacker-OH were able to penetrate limestone specimens in considerably higher, reaching 48.15% an increase of strength values followed 39.84% strength of specimens with Polymethyl methacrylate. It is suggested that very light and viscous consolidant of Wacker-OH and Polymethyl methacrylate could penetrate into the smaller pores of Helwan

limestone gradually, while the penetration of Acrylate was less effective.

varies increment of density after treatment according to the consolidants product maximum increase reached up to 5.61 % after the second cycle of consolidation by Wacker-OH. Ultrasonic sound velocities reflect better the consolidating effect of various consolidants with various longitudinal waves from one agent to the second. All values show a distinct increase after the treatment, Polymethyl methacrylate consolidant has the highest incensement of longitudinal wave comparing with all agents whereas Acrylate has the less longitudinal wave after first and second saturation cycle among whole consolidant types. Aliphatic uretan resin

(Z.K.F) become the first in longer longitudinal waves after second saturation cycle. As the absorption profiles obtained an initial phase with a high absorption rate of untreated 3.28% during the first 2 minute compering with consolidated samples. silica acid ester Wacker-OH presents the lowest water penetration after 24 hours 1.93% followed Polymethyl methacrylate (B-72) 3.13%.

The conducted research proves that, there is need to more others evaluation test. The selection of materials and consolidant must be tailored to the specifics of each treatment, type and Characteristics of rocks mineralogy concerns, and also taking into consideration the environment to which it will be exposed and cultural context. No one consolidant is absolutely preferable. The choice can only be made after laboratory tests to ascertain what product and technique will provide the most satisfactory improvement to the stone's resistance with fewest drawbacks Ethical value which must not be omitted either.

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