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HYDROPHOBIC CONSOLIDANTS FOR TREATMENT OF GRANITIC SCULPTURES AT TELL BASTA, EGYPT: A CASE STUDY

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Abstract

Granite is one of the most common ornamental stones that were widely used in the areas of construction and sculpture in ancient Egypt. It is characterized by its high hardness, good polish, durability, and different colors. Granitic sculptures at Bubastis have been subjected to many deterioration factors, which have adversely affected them in heavy damage symptoms such as weathering, fissures, salt efflorescence, brittleness, microbial contamination, and loss of original features. In the current work, four types of commercial consolidants were evaluated to specify the consolidant of choice for the treatment of the studied granitic statue. Analytical study of the studied granitic statue was performed using x-ray diffraction analysis, polarizing microscope, and scanning electron microscope. The characteristics of the treated granitic samples were studied through colorimetric measurements, measuring of static water contact angle, abrasion resistance, and scanning electron microscope. The results declared that the polymer Aqua mix is the best consolidating material for the remediation of the granitic statue under consideration.

***Keywords**: Hydrophobic; Consolidation; Granite; Bubastis; Tell Basta.*

Introduction

Tell Basta (Bubastis) is considered one of the most important ancient Egyptian cities that is located in the southeastern section of Nile Delta, in the modern city of Zagazig, Egypt (Fig. 1). In ancient Egypt, Bubastis was the home of the cat goddess Bastet, who was the daughter of the Sun God. However, Bubastis was occupied during the different periods of Egyptian history, it attained its greatest importance in the third intermediate period (22^{nd} dynasty), and became the capital of the 18^{th} Lower Egyptian Nome in the late period [1].

The temple of Bastet represents the most important structure in the archaeological city Bubastis. It is mainly constructed from red granite and contains many granitic sculptures [2]. Unfortunately, archaeological elements of the temple are destroyed and many of the granitic sculptures have been exposed to high damage processes.

Granite is one of the most common ornamental stones that were widely used in the fields of construction and sculpture in ancient Egypt. It is characterized by its high solidity, good polish, durability, and various colors. Aswan quarries were the main sources of granite in ancient Egypt [3].

The case study is a granitic statue of Ramesses II accompanied by the god Amun-Ra (Fig. 2) that was discovered in the temple of Bastet. The statue has been subjected to aggressive deterioration factors such as variation in temperature, solar radiation, moisture, rain, dusty

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winds, and air pollutants. Due to the previously mentioned deterioration factors, the studied statue was manifested by numerous physicochemical and mechanical deterioration symptoms such as fragmentation, scaling, fissures, efflorescence, brittleness, and loss of its original features [4-10].

Fig. 1. The site of Tell Basta, Zagazig City, Egypt
(After: Eva Lannge-Athinodorou, 2011)[1]

Fig. 2. Front and back views of the studied granitic statue of Ramesses II (A) accompanied by the god Amun-Ra at Tell Basta (B)

To reduce the harmful effects of the mentioned deterioration factors on the studied monument, it must be consolidated by suitable reinforcement materials, which bind the loose grains and reinforce the surficial layer [11].

Since water is the major damage factor of stone monuments, the consolidation materials must be hydrophobic to protect them from the deleterious impacts of water [12, 13].

The present experimental study aims to evaluate the efficiency of some organic polymers, to determine the optimal hydrophobic consolidant that can efficiently consolidate and protect the studied granitic statue. Analytical study of the studied granitic statue was accomplished using x-ray diffraction analysis, polarizing microscope, and scanning electron microscope. The properties of the treated granitic samples were assessed using colorimetric techniques, measuring of static water contact angle, abrasion resistance, and scanning electron microscope.

Experimental

Materials

Small granitic samples were carefully taken from the fragments fallen from the studied statue. Also, granitic blocks were collected from the granite quarries at Aswan. The granitic blocks were cut into cubic samples (3 and 5 cm^3). The polymers used in the consolidation of granitic samples are: (i) MTMS (Sigma aldrich, Germany) methyltrimethoxysilane; (ii) Aqua mix penetrating sealer (Aqua mix Inc, America) potassium methyl siliconate; (iii) Acrisil 201/o.n (CTS Company, Italy) acrylic and siliconic resin; (iv) Paraloid B72 (CTS Company, Italy) ethyl methacrylate and methyl acrylate.

Methods and Stone Characterization

The samples of the studied statue were characterized using polarizing microscope, x-ray diffraction analysis, and scanning electron microscope. Petrographic examination of the thin sections of granite specimens was performed by Nikon eclipse polarizing microscope.

The mineral constituents of the samples were determined by x-ray diffraction analysis, which was achieved using Philips analytical x-ray Diffractometer, with the following operating settings:- *Diffractometer Type: PW1840, Tube anode: Cu, Generator tension (KV): 40, Generator Current (mA): 25, Wavelength Alpha1(Å): 1.54056, Wavelength Alpha2(Å): 1.54439, Intensity ratio (Alpha2/Alpha1): 0.500, Receiving slit: 0.2, Monochromator used: NO*.

VEGA3 TESCAN scanning electron microscope was used to examine the microstructure of studied granitic samples.

Procedures of Consolidation

In order to perform the experimental study, the cubic granitic samples were washed by distilled water and dried in a hot oven at 105°C for at least 24 hours till reaching constant weight, then allowed to cool at room temperature and controlled relative humidity (RH) 50%, then weighed before treatment. After that, the samples were treated with the polymers by using a soft brush. The treated samples were left for 1 month at room temperature to allow the polymerization process to occur, then the samples were reweighed, and the polymer uptake by the samples was calculated (Table 1).

Table 1. The amounts of polymer uptake in treated granitic samples (in percent)

Polymer	Polymer uptake (%)
MTMS	0.07
Aqua mix	0.04
Acrisil 201/o.n	0.06
Paraloid B 72	0.06

Evaluation of Consolidants

The general appearance of the treated samples was estimated by colorimetric analysis. The colorimetric measurements were performed on both the treated and untreated granitic samples, on homogenous spots, by using Optimatch 3100, based on the L*, a* and b* coordinates of the CIELAB color system [14, 15].

Water repellency of the coated samples was assessed via measuring the static water contact angle using Drop master DM-701, fully automated contact angle meter [16].

The mechanical properties of the treated and untreated samples were determined by testing their abrasion resistance using Bohme abrasion wheel 1006 [17].

VEGA3 TESCAN scanning electron microscope was employed to examine and evaluate the morphology and microstructure of the processed samples.

Results and discussion

Petrographic Study

The petrographic study revealed that the studied granitic samples are composed of microcline, quartz, plagioclase, and biotite. Furthermore, it was clarified that the statue has been exposed to high physiochemical weathering, as feldspars and biotite suffered from alteration to sericite and clay minerals. Moreover, quartz, feldspars, and biotite exhibited mechanical aspects such as cracks, pits, and corrosion (Fig. 3).

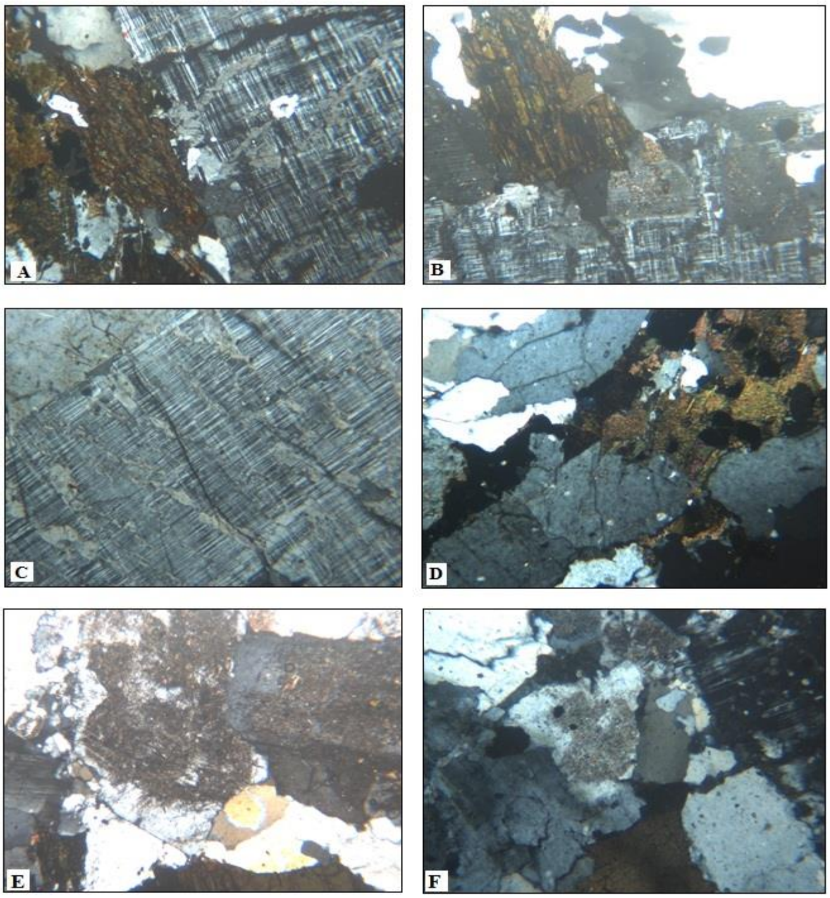

Fig. 3. Photomicrographs of the studied granitic samples. (A) crystals of microcline, quartz, and weathered biotite; (B) grains of microcline, quartz, very weathered biotite, and altered plagioclase; (C) surficial corrosion and cracks in microcline; (D) cracking in quartz, orthoclase, and plagioclase; (E) high alteration of orthoclase and plagioclase to clay minerals; (F) alteration of orthoclase to sericite. (Crossed nicols-magnification 25 X)

Mineralogical characterization

The studied granitic samples were analyzed through x-ray diffractometer. XRD analysis declared that the samples are consisting of quartz, albite, microcline, and biotite. Furthermore, sericite, gypsum, and hematite were detected as weathering products. The results of the mineralogical analysis are reported in Table. 2.

The presence of sericite is attributed to the physiochemical weathering processes, which cause the partial alteration of biotite and potassium feldspars (microcline and orthoclase) into sericite [18]. The existence of gypsum is attributed to the reaction between sulfuric acid and Ca-bearing feldspars. Sulfuric acid results from the combination of water and sulfur dioxide [19]. Hematite is formed after the leaching of ferrous-ferric ions from the crystal structure of biotite at the beginning of the weathering process [20].

Table 2. Mineralogical constitution of the studied granitic sample

Minerals	Sample 1
Quartz	40.50 %
Microcline	17.10 %
Albite	26.34 %
Biotite	03.83 %
Sericite	04.50 %
Gypsum	04.16 %
Hematite	03.57 %

Scanning electron microscope

Based on the SEM micrographs (Fig. 4), the studied granitic samples were found to suffer from many deterioration aspects such as accumulation of weathering products, granular disintegration, salt crystallization, pitting, and microcracking.

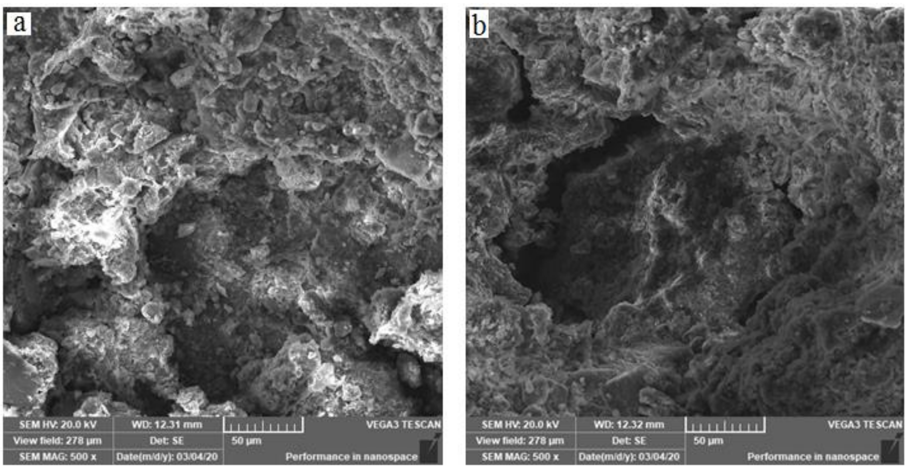

Fig. 4. (a, b) SEM micrographs of the studied granitic sample

Color Alteration

The color alteration of the treated granitic samples was evaluated using colorimetric analysis. The chromatic alterations (ΔE^*_{ab}) were performed using Optimatch 3100 to calculate and assess the color change caused by the treatments, using the following formula [14, 15]:

$$\Delta E^{*}{}_{ab} = \sqrt{(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2}} \quad ,$$

where: ΔL*, Δa*, and Δb* are the variances in the, L*, a*, and b* coordinates (according to CIELAB color system) of the processed and unprocessed granitic specimens. The results of chromatic measurements of the granitic samples demonstrated that the polymers of Aqua mix and MTMS achieve the best results, as they do not have any influence on the colors of the treated samples. The polymer of Paraloid B72 caused a slight change in the color of the treated sample, while Acrisil 201/o.n. resulted in a noticeable variation in the color. Table 3 shows the results of the colorimetric analysis for the treated and untreated granite samples.

Table 3: Chromatic measurements of the treated samples

Consolidant	ΔE
MTMS	3.25
Aqua mix	2.95
Acrisil 201/o.n	9.30
Paraloid B 72	5.90

Hydrophobicity

Water represents the key factor in the deterioration of stone monuments, especially in open environments. It plays a significant role in the decomposition and mineralogical alteration of granite. Besides, it catalyzes the physiochemical and microbiological deterioration processes [21].

Therefore, the consolidants used in the treatment of granitic monuments must be hydrophobic. The hydrophobicity of the processed granitic samples was estimated by measuring the static contact angle (sessile-drop method). Each sample was tested at least 3 times in different positions, and then the mean values were calculated [22]. Based on the results of static contact angles, all consolidants used in this work improved the water repellency of the granitic samples. The silicon-based consolidants (Aqua mix and MTMS) produced good hydrophobic properties, as they achieved higher degrees of static contact angles, this is due to the presence of the non-polar alkyl groups that possess hydrophobic properties [11].

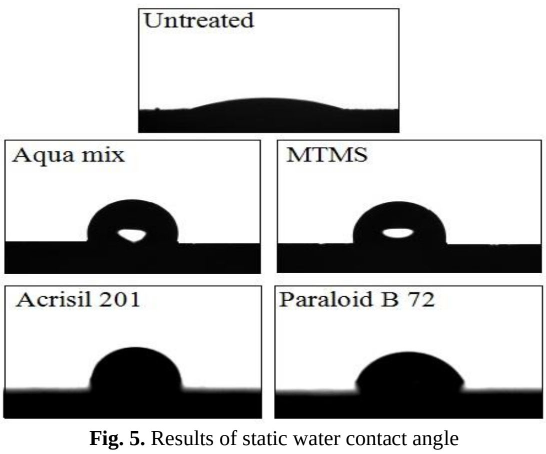

Fig. 5. Results of static water contact angle

The polymer of Paraloid B72 is considered to be hydrophilic material, as it achieved static contact angles less than 90º. Figure 5 and Table. 4 represent the results of static water contact angle.

Table 4. Static contact angles of treated and untreated granitic samples

Consolidant	SCA (º)
Untreated sample	18.5 °
Aqua mix	112 °
MTMS	109 °
Acrisil 201/o.n	90.1 °
Paraloid B 72	59.5 °

Abrasion Resistance

The efficiency of the used consolidants in improving the mechanical properties of the treated granitic samples was estimated by testing the abrasion resistance of the processed and unprocessed samples using the machine Bohme abrasion wheel 1006. In this test, the abrasion resistance is determined by calculating the percentage of the loss in weight in the granitic samples. The results are summarized in Table 5.

The consolidants of Paraloid B 72 and Acrisil 201/o.n achieved the best results in abrasion resistance due to the high adhesive action of acrylic polymers, which enables them to efficiently enhance the mechanical properties of the stone [23, 24].

Table 5. Rates of the loss in weight for treated and untreated granitic samples.

Consolidant	loss in weight (%)
Untreated sample	2.05
Aqua mix	1.73
MTMS	1.62
Acrisil 201/o.n	1.54
Paraloid B 72	1.35

Scanning Electron Microscope

The scanning electron microscope was utilized to investigate the morphological features of the treated granitic samples. SEM micrographs (Fig. 6) showed that the consolidants of Aqua mix and MTMS coated the samples with a thin polymeric film, without closing the tiny pores.

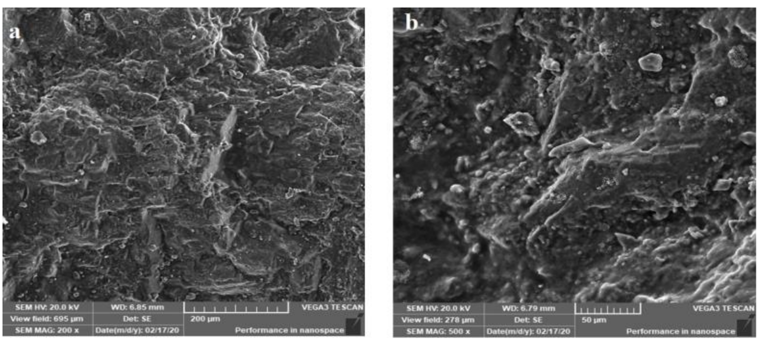

Fig. 6. SEM micrographs of the granitic samples treated with (a) Aqua mix; (b) MTMS

The consolidant of Paraloid B 72 had coated the samples with a homogenous, dense layer (Fig. 7a), while the consolidant of Acrisil 201/o.n coated the samples with a dark, dense coat, containing many inhomogeneous spots (Fig. 7b), which may be caused by the heterogeneity in the composition of that product, as it consists of acrylic and siliconic resins.

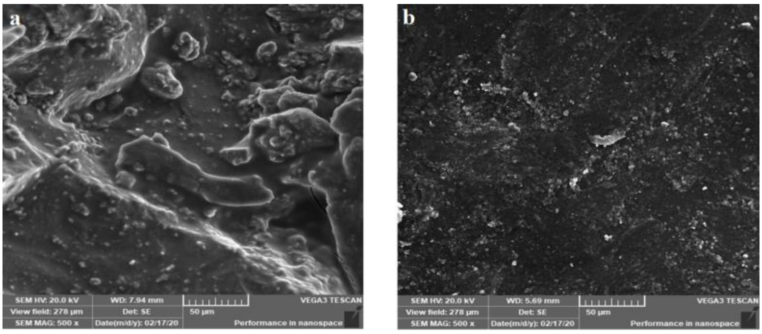

Fig. 7. SEM micrographs of the granitic samples treated with (a) Paraloid B 72; (b) Acrisil 201/o.n

Conclusions

The temple of Bastet is an important and well-known archaeological site in the ancient city of Bubastis. It contains a large number of granitic sculptures and archaeological elements that have been subjected to serious deterioration processes. The studied statue of Ramesses II has suffered from numerous physicochemical and mechanical deterioration signs such as granular disintegration, fissures, staining, salt efflorescence, brittleness, and loss of its original features.

In the current work, four types of six commercial consolidants were evaluated to determine the best of them for the treatment of the studied granitic statue. The colorimetric analysis showed that the consolidants of Aqua mix and MTMS did not cause any alteration of the colors of the processed samples. The polymer of Paraloid B72 caused a mild change in the color of the processed sample, while Acrisil 201/o.n. resulted in significant darkness in the color. In addition, it was observed that the silicon-based consolidants (Aqua mix and MTMS) possess better hydrophobic properties, as they achieved higher degrees of static contact angles. The consolidants of Paraloid B 72 and Acrisil 201/o.n provided the best values in abrasion resistance due to the better adhesion properties of acrylic polymers.

Based on the reported results, it can be suggested that Aqua mix is the optimal consolidant for treatment of the studied granitic statue, as it provided the lowest value in the color change; and showed the greatest efficacy of water repellency; in addition to the acceptable value of abrasion resistance. Moreover, it did not cause the total closure of the pores in the surficial layer, as observed from SEM micrographs.

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