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EXPERIMENTAL STUDY FOR THE CONSOLIDATION AND PROTECTION OF SANDSTONE PETROGLYPHS AT SARABIT EL KHADEM (SINAI, EGYPT)

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ABSTRACT

This research aims to determine the optimum material in the consolidation and protection of the sandstone petroglyphs at Sarabit El Khadem, Sinai, which are considered one of the most important features of ancient Egyptian civilization. For this purpose; four commercial products were used in the treatment of sandstone samples that were collected from the archeological site of Sarabit El Khadem. The properties of the treated sandstone samples were evaluated using different methods such as colourimetric measurements, static water contact angle, total immersion water absorption, compressive strength, and scanning electron microscope. The results demonstrated that the product of PF4 has a significant efficiency in the consolidation and protection of the sandstone samples.

KEYWORDS: consolidation; protection; static water contact angle; hydrophobic; sandstone; petroglyhs; Sarabit El Khadem; Sinai.

1. INTRODUCTION

Petroglyphs are one of the important archaeological features, as they include a lot of historical and technical information about ancient periods. In Egypt; petroglyphs are widely spread in many archaeological sites, especially in ancient stone quarries. Sarabit El Khadem is an important archaeological site that locates at Sinai; the site contains numerus petroglyphs on the sandstone mother rock spreading in that area (Nour El Din, 2010). Sandstone was used in constructing and sculpting many ancient Egyptian monuments, this sedimentary rock is significantly affected by weathering process, which affects not only the aesthetical appearance, but also results in internal structural damage. In addition, due to the high porosity of the sandstone; it is easily attacked by water from its different resources, such as rain, relative humidity, and groundwater, which cause many deterioration aspects (Fig. 1), such as granular disintegration, exfoliation, detachment, as well as cracking, efflorescence, discolouration, different microbiological colonization (Amoroso and Fassina, 1983; Saleh, et al., 1992; Abd El-Hady, 2000; Fitzner, et al., 2003; Turkington, et al., 2003; Hosono, et al. 2006; Jain, et al. 2009). This research aims to prevent the damage process of the sandstone petroglyphs at Sarabit El Khadem, Sinai; it also aims to select the most suitable consolidant and protective materials (Tsakalof, et al., 2007; Darienzo, et al., 2008; Bader 2014).

2. MATERIALS AND METHODS

Sandstone samples were prepared into cubic samples (2.5, 3, 5 cm^3), the cubic samples were washed by distilled water, and then dried at 105 °C for 24 hours to reach constant weight, then left to cool at room temperature with RH 50%, then weighed again. Four types of ready to use products were used for consolidating and protecting the sandstone samples. The materials used are: (1) Estel 1000 (CTS Company, Italy); (2) penetrating sealer (Aqua mix Inc, America); (3) Acrisil 201/o.n (CTS Company, Italy); PF4 (Chem Spec Company, Italy). The chemical compositions of the used products are reported in Table (1).

Table 1: The chemical compositions of the used products

product	Composition	Solvent
Estel 1000	Ethyl silicate	White spirit
Penetrating sealer	Potassium methyl siliconate	Water
Acrisil 201/o.n	Acrylic and Siliconic resins	Thinner AC 204
PF4	alkyl alkoxy silane modified titanium dioxide nanoparticles	Water

The products were applied onto sandstone samples by brush for three applications, and then the treated samples were left for one month at room temperature and controlled RH 50% to allow the polymerization process to take place.

The petrographic study was performed using Nikon eclipse LV100POL polarizing microscope. The mineralogical composition was determined by X-ray diffraction analysis, which was performed using Philips Analytical X- Ray Diffractometer. The operating conditions were: 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. The chemical analysis was carried out using X-ray fluorescence (Axios spectrometer, PANalytical Company, Netherlands).

The aesthetical properties of the treated sandstone samples were evaluated by colourimetric examination. The colourimetric measurements were carried out on the treated and untreated sandstone samples, on homogenous spots, by means of Optimatch 3100, based on the L*, a* and b* coordinates of the CIELAB colour space (Schanda, 2007). The water repellency of the treated samples was evaluated by carrying out the test of static water contact angle using Drop master DM-701, fully automated contact angle meter. The rates of water absorption for the treated sandstone samples were calculated according the gravimetric method, in which the treated and untreated sandstone samples were completely immersed in distilled water at room temperature, then the samples were taken out after 24 hours, carefully wiped with tissue paper and weighed immediately. Finally the amount of the absorbed water was calculated using the following equation:-

$$\text{Water absorption} = \frac{(W_2 - W_1)}{W_1} \times 100 = \cdots\cdots \%$$

Where (W_2) is the mass of the sample after immersion in water for 24 hours, and (W_1) is the mass of the sample before immersion. Mechanical properties were evaluated by testing the compressive strength of the treated and untreated samples according to ASTM C 170. Morphological aspects of the treated and untreated sandstone samples were evaluated using Inspect S scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. *STONE CHARACTERIZATION*

The petrographic study revealed that the studied sandstone samples can be classified as quartz arenite, as they mainly formed of more than 95% quartz. The quartz minerals spread in the samples as rounded and sub-rounded grains slightly or weekly cemented by iron oxides and clay minerals (kaolinite) as later detected by XRD. Fig. 1 shows the thin sections of sandstone samples under polarizing microscope. Previous results were confirmed by the X-ray diffraction pattern which showed that the sample is mainly composed of quartz, with trace amounts of microcline and kaolinite, as shown in Fig 2.

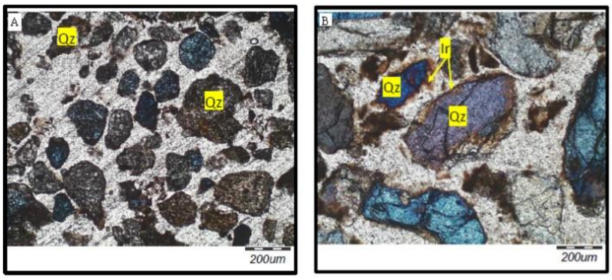

Figure 1. (A) Poorly-cemented quartz grains with substantial pore-space (Crossed polars); (B) quartz grains surrounded by thin coating of iron oxide, (Crossed polars)

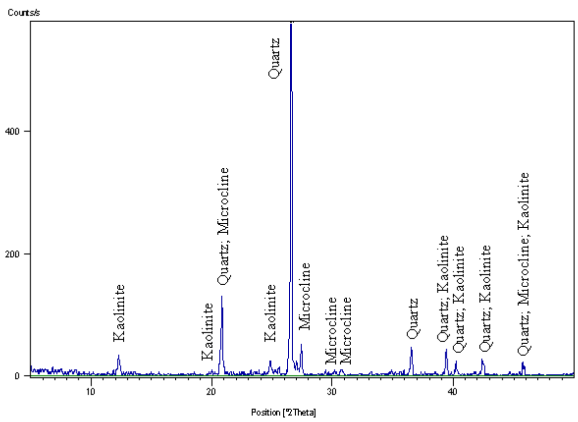

Figure 2. X-ray diffraction pattern of the studied sandstone

The results of X-ray diffraction clarified that the binding material of the studied sandstone mainly consists of clay minerals (kaolinite) which make the sandstone more susceptible to damage processes. This is due to the high tendency of clay minerals to water absorption, which results in many deterioration aspects such as granular disintegration, cracking, and flaking off (Fitzner, et al., 2003). The results of chemical analysis that was performed using X-ray fluorescence confirmed the results obtained by x ray diffraction analysis. The results are shown in Table (2).

Table 2: Chemical composition of the sandstone sample

Main constituents	Concentration (%)
SiO2	93.9755
Fe2O3	1.1411
Al2O3	1.1259
CaO	1.3362
MgO	0.0304
P2O5	0.1003
Na2O	0.3009
K2O	0.0258
Cl	0.0102
SO3	0.0084
MnO	0.2153
TiO2	0.1887
L.O.I	1.5186

3.2. *COLOUR ALTERATION*

In order to assess the variation in the aesthetical properties induced by the treatments, colour alteration test was performed by means of Optimatch 3100, according to the following equation:-

$$\Delta E = \sqrt{[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2]}$$

Where ΔL*, Δa* and Δb* are the differences in the, L*, a* and b* coordinates (according to CIELAB colour system) of the treated and untreated sandstone samples. The values obtained from the chromatic measurements of the sandstone samples (Table. 3), demonstrated that the product of PF 4 achieve the best results, as it hadn't a noticeable effect on the colour of the treated samples. The products of Estel 1000 and Penetrating sealer caused a slight change in the colour of the treated sandstone, while the product of Acrisil resulted in a significant colour alteration.

Table 3: The chromatic measurements of the treated samples

Treatment	L*	a*	b*	ΔE*
Untreated	49.00	8.80	9.12	
Estel 1000	41.97	9.64	8.71	6.78
Penetrating sealer	44.10	11.64	9.87	5.38
Acrisil201/o.n	46.83	9.94	9.45	14.60
PF4	48.81	8.71	9.42	0.28

3.3. *STATIC WATER CONTACT ANGLE*

Hydrophobicity is considered one of the most important properties of the consolidation and protective materials (Helmi and Hefni, 2014). The hydrophobicity of the treated sandstone samples was determined by measuring the static contact angle of water droplets that were placed on different positions on the samples. The static water contact angle (SCA) of the untreated sandstone sample was zero^o, as the water droplet penetrates inside the pores. The results confirmed that all products used in this study modified the static water contact angles of the sandstone samples. The results demonstrated that the polymers of Estel 1000 and Acrisil are hydrophilic materials, as they have contact angles less than 90 degree. Also it was found that the polymer of Penetrating sealer is a hydrophobic material, as it achieved contact angles more than 90 degree. The hydrophobic properties of this polymer resulted in the presence of non-polar alkyl group connecting to the silicon atoms.

PF 4 achieved the highest degrees of contact angles, this is due to the hydrophobic properties of alkyl alkoxy silane, the backbone polymer in this nanocomposite (Helmi, and Hefni, 2016), in addition to the surface roughness resulting from titanium nanoparticles, that lead to trapping of air between water droplets and the rough surface, which is illustrated in the Cassie-Baxter scenario (Cassie and Baxter, 1944). The results are summarized in Table (4) and Fig.3.

Table 4: Static contact angle of treated and untreated sandstone samples

Treatment	SCA (º)
Untreated sample	0 º
Estel 1000	73 º
Penetrating sealer	98 º
Acrisil 201/o.n	85 º
PF4	126 º

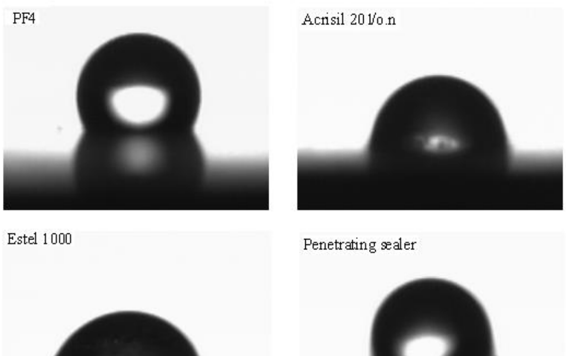

Figure 3. Static contact angle photographs of the treated and untreated sandstone samples

3.4. *WATER ABSORPTION*

Reducing water absorption rates of the treated samples is an important aim that has to be achieved by consolidants and protective materials. By measuring the water absorption values of the treated and untreated samples, it was found that the four materials used in this study led to reduce water absorption rates of the sandstone samples; this is attributed to the ability of these products to improve the physiochemical properties of the sandstone. It was also found that the materials which have non-polar alkyl groups (Penetrating sealer, PF 4) achieved the best result in reducing the rates of water absorption of the treated samples. These results confirmed that the amount of the water absorbed by the treated samples mainly depends on the chemical composition of the used polymer. Table (5) shows the average values of water absorption for the treated and untreated sandstone samples.

Table 5: Results of water absorption of the treated sandstone samples

Treatment	Water absorption (%)
Untreated	9.20
Estel 1000	5.20
Penetrating sealer	1.30
Acrisil 201/o.n	3.40
PF4	1.05

3.5. *MECHANICAL PROPERTIES*

As expected, all products used in this study achieved considerable improvement in compression strength. The products of Estel 1000, Penetrating sealer and PF 4 achieved Convergent values of compressive strength; this can be attributed to the similarity in their natures which depend on silicon polymer that contains an inorganic polar side (Si-O bonds). As a consequence, the polar side provides the polymer molecules with electrical attraction forces which lead to increase the connection between the polymer and the stone components (Torraca, 2009). The product of Acrisil Achieve the highest values in compressive strength. These results indicate that the addition of acrylic polymers to silicon polymers has a positive effect in increasing their mechanical properties; this can be attributed to the good adhesion properties of acrylic polymers which resulted in their relatively high surface free energy (Brus, and Kotlik, 1996). The average values of compressive strength of the treated and untreated sandstone samples are shown in Table (6).

Table 6: Average values of compressive strength for treated and untreated sandstone samples

Treatment	Compressive strength (Kg/cm2)
Untreated	112
Estel 1000	194
Penetrating sealer	236
Acrisil 201/o.n	189
PF4	198

3.6. *SCANNING ELECTRON MICROSCOPE (SEM)*

Inspect S scanning electron microscope was used in order to evaluate the consolidating and protective materials which were used in the present study. From SEM micrographs (figure 4) of the treated and untreated sandstone samples, we can note that the untreated sandstone samples appear in very fragile state, and have many pores. In addition, the quartz grains are significantly disintegrated. Moreover; all the products used in this study succeeded in covering the samples with polymeric networks, in addition to improving the connection between the grains and also filling the big pores. The products of Estel 1000 and Penetrating sealer covered the samples with rough polymeric networks, containing tiny pores. The product PF4 covered the samples with a homogenous polymeric layer, containing a lot of tiny individual nano aggregates, while the product Acrisil 201/o.n covered the samples with non-homogenous dense coat, which suggested to be caused by the heterogeneity in the composition of that product, as it consists of Acrylic and Silicon resins.

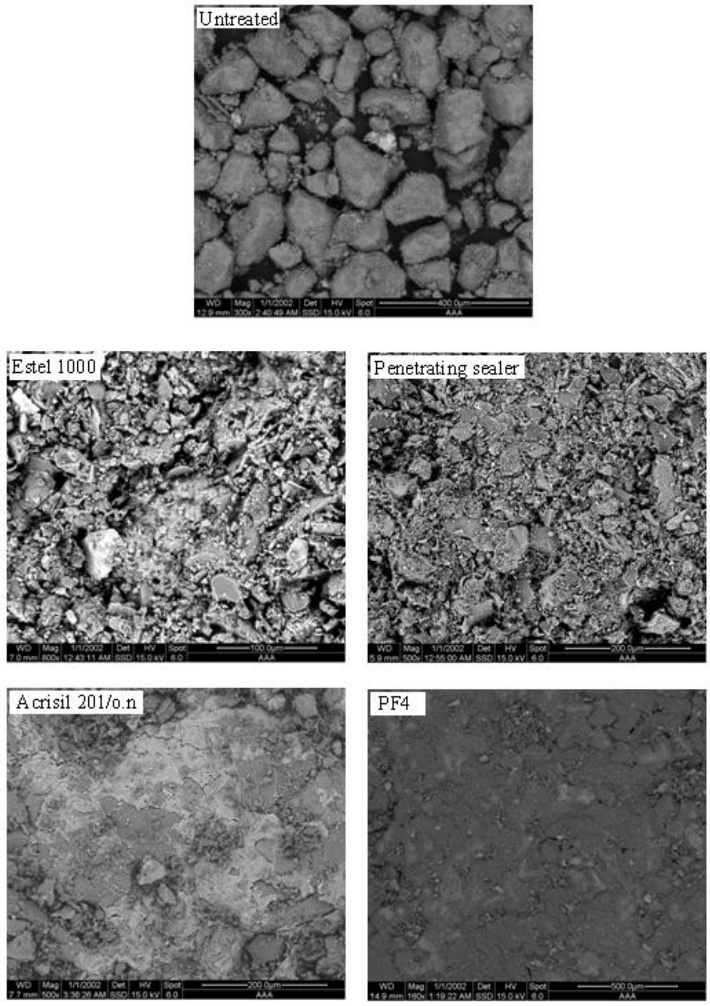

Figure 4. SEM micrographs of the treated and untreated sandstone sample

4. CONCLUSIONS

Sandstone petroglyphs at Sarabit El khadem are suffering serious deterioration factors including wind erosion, salt weathering, variation of air temperature and humidity, therefore; these petroglyphs became fragile and brittle. The colorimetric measurements demonstrated that the product PF 4 didn't cause any effect on the color of the treated sandstone samples. The products of Estel 1000 and Penetrating sealer led to slight change on the color of the samples, while the product of Acrisil 201/o.n resulted in a significant color change. PF 4 is the most suitable product for the consolidation and protection of the sandstone petroglyphs of Sarabit El Khadem, as it has a good effect in improving the mechanical properties of the treated sandstone samples, in addition to its ultra-hydrophobic properties that were determined by the test of static contact angles. Moreover, SEM micrographs demonstrated that the product PF 4 had the ability to cover the quartz grains with a homogenous layer.

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