

## Effectiveness Assessment of Nano Silicate Application to Improve Mechanical Properties of a Limestone Used in the Architecture of Pasargadae World Heritage Site

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### 1-Introduction

Stone is one of the raw building materials, which has long been used. Stone has always been important in construction due to its physical and chemical resistance in general and its durability in particular.

In this study, we consider one of the most important historical monuments of Iran; The Pasargadae World Heritage Site. Pasargadae WHS is located in Dasht-e Morghab, Fars province. The stones used in Pasargadae monuments have three different texture and colors (beige, green-gray and dark-gray) which were recognized as a limestone. The beige stone is a type of pure limestone with a low rate of dolomite. Dark-gray stone is argillaceous limestone and the green-gray stone is sandy limestone. The green-gray stone is vulnerable to weathering and has been affected by it and its decay pattern is sandy and in some parts it has totally been destroyed. Given the intensity of its deterioration, we aim to consolidate the green-gray stone.

Through stone consolidation, various specialists from engineering sciences have assisted the conservators to provide proper materials for preservation of historical monuments. In order to increase the durability green-gray stone against further weathering, we tried to figure out the treatment effect on the stone durability by evaluating one of the improved materials, which has been strongly recommended in relevant recent investigations. In order to assess the efficiency of the treatment, we used methods drawn from civil engineering sciences to measure the changes and improvements of the mechanical properties of the stones.

In this study, based on laboratory studies, an analytical-experimental method was used to evaluate the efficiency of the consolidation material on the green-gray stone known as "sang-e kaboud" from the Pasargadae WHS.

### 2-Experimental Program

The consolidation treatment was conducted with Nano

ESTEL®, C.T.S. dispersion in water (dilution 1:10) on samples from the quarry and the procedure was conducted using brush until imbibition of the substrate.

In order to evaluate the hydric parameters, mechanical resistance and mechanical properties of treated stone, some experiments were including water absorption, water capillary absorption, water vapor permeability coefficient, porosity and surface strength were conducted. Water absorption at the atmospheric pressure was measured following the UNE-EN 13755 standard. We also measured the degree of interconnection between the pores and the saturation coefficient. Measuring the drying rate was obtained by following NORMAL 29/88, 1991. Capillary absorption coefficient of water and vapor permeability coefficient were determined following UNE-EN 1925, and the UNI, E. 15803, respectively.

The treatment efficiency was evaluated in terms of superficial consolidation with *micro-drilling* test by Measuring System (DRMS) Cordless drill with a flat-edged 5-mm diameter bit with a diamond-covered tip. Also, freeze-thaw and salt crystallization accelerated aging tests were carried out to evaluate the durability of the stone. UNE-EN 12371 standard was employed for the freeze-thaw test for 70 cycles. The damage caused by salts was analyzed according to the UNE-EN 12370 standard. The environmental conditions in the laboratory were 20 °C and 30 ±5% of relative humidity in both tests.

The compactness of the stone was evaluated by ultrasounds during the cycles of aging test (every five cycles) using a Panametrics HV Pulser/Receiver 5058PR coupled with a Tektronix TDS 3012B oscilloscope under controlled thermo-hygrometric conditions (~20 °C and the relative humidity of ~35%) in accordance with the ASTM D 2845-05.

For the macroscopic observation of micro-cracks and the decay pattern during the aging, we used a Leica video-microscope with the model DVM2000 (DVM) with a 50-400x lens (and a corrective lens of 0.4x).

### 3-Result and Discussion

The comparison of water absorption of intact and treated samples indicates 11 percent of decrease in water absorption rate. The porosity obtained from the hydric tests (HT) turned out to have 14 percent decrease in porosity. The interesting point is that the slope of water absorption after the treatment is sharper than the untreated samples. This phenomenon is due to changes in the pore size. However, the slope of water drying test indicates that the treated stones dried slowly in comparison with the intact stone. It is clear that the pore system is responsible for different drying speeds. Slower

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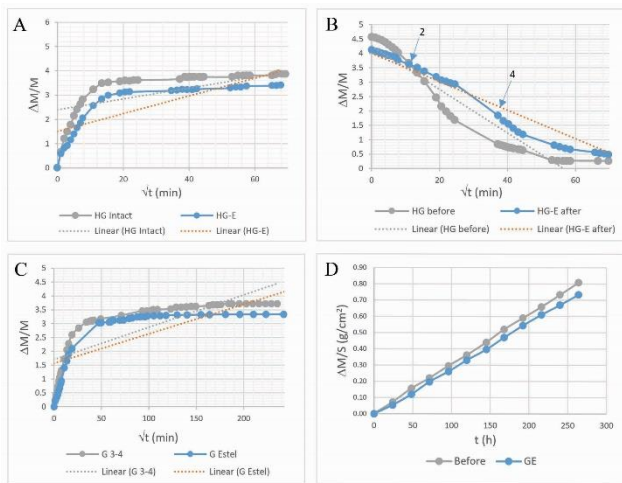
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drying means that water is longer retained in the stone pore system; therefore, this can affect the stone durability. This phenomenon happens when the water solution of silica nanoparticles exposed to high RH gives rise to a final solid product of hydrated amorphous silica that behaves in a similar fashion like silica gel.

The water capillarity uptake of the intact stone takes place faster than treated stone (almost one-half). Also, the treated samples stopped absorbing and achieved mass saturation while the intact stone was absorbing at that time. This phenomenon shows that some pores and capillaries are clogged by the nanoparticles of silica.

Water vapor permeability shows a similar behavior for both stones (untreated and treated). However, the treated stone has a slight slope, which is indicative of the clogged pores. It is obvious that the pores tortuosity, which is a relevant factor to the water vapor permeability of the stone, has not changed (Fig. 1).



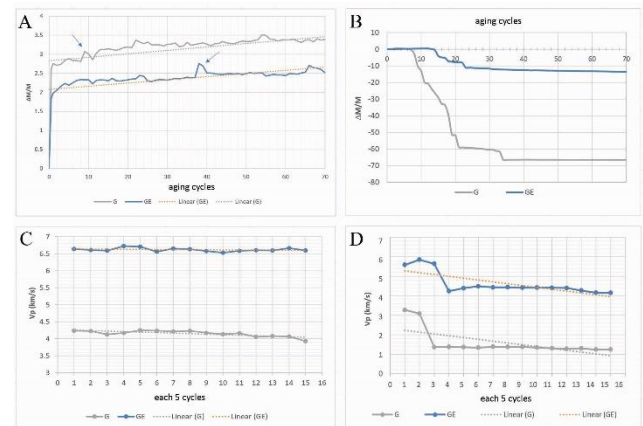
**Fig 1. A) Water absorption curves; B) Water drying curves; C) Water capillarity absorption; D) Water vapor permeability lines**

The results of resistance to micro-drilling showed that a substantial increase in resistance about 2 N/mm is acceptable by considering the low dilution of consolidation material.

The freeze-thaw test did not cause any noticeable damage and no substantial changes in the weight of the samples were observed. The location of one micro-crack in the aging curves was, however, changed. In the intact sample curve, the pick of micro-crack occurs at the tenth cycle while in the treated sample, it occurs at the 39<sup>th</sup> cycle (Fig. 2). The salt-crystallization test had very damaging effects on intact samples and it showed a substantial resistance in the treated stone. Intact samples lost 60 percent of its weight while treated samples lost 20 percent of its weight at the end of the aging cycles.

The measurement of the velocity of propagation of ultrasonic waves allows us to assess the degree of compactness of the stones as the speed of propagation depends directly on the percentage of the pores, the type and volume of the fissures, the density and composition of the minerals, the textural anisotropy and the humidity present. According to the aforementioned point, the

propagation velocity of untreated and treated samples during freeze-thaw shows the velocity of  $V_p$  in the treated samples is more than the in untreated stone, indicating the decrease of pores percentage and increased compactness. The propagation velocity of untreated and treated samples during salt crystallization test indicated that nanoparticle of silica increased the resistance against salt crystallization for only ten cycles more than the intact stone (Fig. 2).



**Fig 2. A) Weight loss evolution of freeze-thaw aging test; B) Weight loss evolution of salt crystallization test; C) Ultrasound velocity variation of freeze-thaw aging; D) Ultrasound velocity variation of salt crystallization aging**

#### 4-Conclusions

Consolidation limestone by Nano silicate highlight some advantages and one disadvantage:

The advantages include improving two properties of the stone (porosity and superficial resistance) as well as the resistance against accelerated aging tests (freeze-thaw and salt crystallization) by considering the dilution of material, which help to increase sandy limestone durability used at Pasargadae World Heritage Site.

The negative point of Nano silicate treatment is the reduction rate of drying which should be considered in further research.