

AN EXPERIMENTAL STUDY CONDUCTED TO DETERMINE THE EFFECTIVENESS AND DURABILITY OF PRESERVATION TREATMENTS ON VOLCANIC TUFF STONES

Seden ACUN ÖZGÜNLER¹, Zeynep Sena KARKAŞ^{1*}

¹ Istanbul Technical University, Department of Architecture, Taksim, Istanbul, Turkey

Abstract

In this study, two treatments were performed on deteriorated volcanic tuff stone samples taken from a 16th-century historical structure: (i) solventless mixtures of ethyl silicates (TEOS) tetraethoxysilane consolidation product followed by application of two different silane-siloxane-based water-repellent commercial products (TEOS+WR1 and TEOS+WR2), (ii) two different silane-siloxane based water repellent commercial products (one emulsion (WR2) and the other solution (WR1) based). This study aims to determine the effectiveness, compatibility, durability and service life of the studied conservation treatments on tuff stones. Therefore, colorimetric measurements, chemical and petrographic analyses (XRF, XRD, SEM-EDS) and physical and mechanical characterization tests were performed on the treated and untreated samples. Additionally, accelerated weathering tests were performed in the laboratory on all treated stones to determine the long-term performance of the chemical treatments. After these weathering tests, physical (water absorption under atmospheric pressure, water capillarity coefficient, water vapour permeability) and mechanical (ultrasonic pulse velocity, flexural and compressive strength) property tests were performed again and according to the results, the performance change in the efficiency indexes (TEI, %) was calculated. All results were compared and discussed. The results showed the best performance of TEOS+WR1 treatment in improving the consolidating and water-repellency abilities of tuff stone samples. However, the least colour change in the colour measurements after the treatments was in the treatments using emulsion-type water-repellent products.

Keywords: Volcanic tuff; State of conservation; Stone consolidation; Water repellent; Chemical treatment

Introduction

From ancient times, the construction of buildings was carried out following bioclimatic design. Local materials were used to ensure the principle of sustainability and to benefit from natural heat energy sources. Thus, the environmental and energy-efficient construction principles of the period were applied. Natural stones have been a critical material in historical buildings and monuments since ancient times. Natural stones' durability and environmental resistance have ensured their sustainability for centuries [1].

Tuff stones are among the natural stones used in historical buildings in different countries. Tuff stones are igneous rocks of volcanic origin. The stone known as "Od stone," a type of volcanic tuff stone, is green dacitic tuff and is the commonly used tuff stone in many historical buildings and monuments in Turkey. These types of tuff stones were used in buildings and repair works in the Roman, Early Byzantine Period (4-6th century) and Ottoman Period (16-20th century) due to their lightweight, easy workability, fire resistance, low energy and

* Corresponding author: karkas17@itu.edu.tr

labour requirement [2]. However, degradation processes adversely affect tuff stones due to their chemical and mineralogical composition, macro-porous texture and poor mechanical properties [3, 4]. Environmental factors such as precipitation, wind erosion, temperature fluctuations, biological decomposition and water-soluble salts (especially in buildings close to the sea) cause decay types such as flaking, erosion and alveolarization on the surfaces of tuff stones [2, 4].

Moreover, the resulting damage is usually the result of interactions of various physico-mechanical mechanisms such as salt crystallization, freezing-thawing and thermal and moisture expansion [5, 6]. Water entering the material for various reasons and in different forms (solid, liquid, gas phases) is the primary damage factor for tuff stones. Water has a very influential role in the degradation mechanisms of tuffs, as it quickly penetrates volcanic tuff material with high porosity and strong hydrophilic character, thus carrying abrasive substances, promoting microbial, dissolving soluble components and creating high tensile stresses when frozen [5, 7].

Due to problems such as the limited life of the quarries and the cost of removing and transporting the stones from the quarries, it has become more critical to preserve the original natural stone materials in the building without changing them during the preservation works. Maintaining authenticity is one of the core concepts of most conservation needs and keeping the authenticity of the original natural stone materials in historical buildings in situ is one of the aims of protecting cultural heritage structures. For this reason, protective chemical treatment methods are used by using water-repellent and consolidant chemical materials to reduce the hydrophilicity of volcanic tuff stones, to prevent biological, chemical and physical mechanisms that cause deterioration and to strengthen the deteriorated stones [8-13]. When there is surface loss in stones, consolidant protective materials are used mainly for the stones that deteriorate due to the loss of binding minerals. These materials are used to improve the cohesion of the stone's mineral components, increase the stone's mechanical resistance by providing cohesion between the degraded areas of different degrees and reduce surface loss [13-15]. In addition, if the water penetrating the stone accelerates the deterioration processes, water-repellent products are used to delay the contamination of the stone, prevent the penetration of water and aqueous solutions into the stone and reduce the deterioration rate of the stone [13, 14, 16]. Additionally, some performance criteria are expected from consolidant and water-repellent chemical materials.

These are the fact that the stones change the water vapour permeability, optical properties and aesthetic properties little or not at all, do not cause biological factors in the stones, increase the durability properties of the stones, be economical and ecological etc. [13-17].

Sustainability from a cultural heritage perspective is about all preventive solutions developed to maintain the desired conditions over the lifetime of the heritage object, thus prolonging its life [18]. Many consolidant and water-repellent products have been used in historical buildings and monuments conservation studies [12, 19]. Alkoxysilane-based products are the world's most well-established and used stone consolidant materials [12]. These products are preferred for volcanic tuff preservation because they create synthetic silica between the pores of the degraded stones. In many studies, it has been stated that treating the surfaces of the stones with a consolidant material first, followed by the second application of water-repellent material to the surfaces of the stones, provides longer-term protection on the stone surfaces [20].

However, in another study, it was determined that using water-repellent materials alone was more successful in conservation studies of volcanic tuffs since it was determined that the water absorption values of volcanic tuffs decreased and the deterioration processes of volcanic tuffs were reduced [21].

Researchers and companies are constantly modifying chemical compositions to improve the performance of alkoxysilane-based treatments or to address environmental and safety issues [11, 12, 22]. Despite this, the vital constituents responsible for the consolidation action in

alkoxysilanes have remained virtually unchanged over time. For this reason, alkoxysilane-based products have been used for over forty years [22]. The most commonly used alkoxysilane precursor in commercial products as a protective material is tetraethoxysilane (TEOS). TEOS has been extensively studied in international research, as it can penetrate the stone matrix [23] and polymerizes through a sol-gel process, forming siloxane chains that bind grains [11, 22-29].

Tetraethoxysilane (TEOS) and alkyl alkoxysilanes lack solubility when used in consolidant or water-repellent product formulations. Therefore, formulations must be applied in organic solvents (VOCs) to be classified as "greener" solvent formulations [30]. VOC (volatile organic compound) regulations mean that any chemical treatment must be formulated to be environmentally friendly. For this reason, protective chemical products must have sufficient VOC levels not to emit harmful chemical gases and can be called "green" solvents [31]. Due to the harmful environmental effects of solvent-based water repellents, emulsions (water-based) formulations were introduced in the late 1980s and were shown as an alternative to solvent-based formulations [32, 33]. Some studies have observed that water-based formulations increase penetration depth in humid environments and perform better in low-porous stones such as granite. On the other hand, a lower performance was obtained compared to solvent-based formulations against freezing-thawing cycles [32, 33]. Additionally, water often scores higher in the solvent classification. Moreover, for this reason, using aqueous methods instead of organic solvents in conservation studies is preferred as the most environmentally friendly and safest approach. However, the full sustainability of these practices is questioned if the high energy cost of chemical treatments is given more importance [34].

The literature research shows that the decay and protection of volcanic tuffs have yet to be studied in detail as sandstone and limestone. Since the deterioration mechanisms of volcanic tuffs are more complex than other stones, consolidation is risky and requires detailed studies. In this study, degraded volcanic tuff samples were taken from a listed historical structure of the 15-16th century located by the sea in Istanbul and the macro and microstructure of these stone samples were determined. Then, two different protective chemical treatments were applied to these deteriorated stone samples (i) solventless mixtures of ethyl silicates (TEOS) tetraethoxysilane consolidation product followed by the application of two different water-repellent commercial product applications, which are a mixture of silane siloxane, (ii) two different water-repellent products, which are a mixture of silane siloxane alone, are emulsion and solution based.

This study aims to investigate the effectiveness of these protective chemical treatments on tuff stones (effectiveness on physical and mechanical properties and microstructure), long-term performance (durability) and compatibility and evaluate the analysis results. In addition, two questions were investigated in this study.

These questions are, (i) is the consolidation followed by the application of water-repellent treatment or are the water-repellent treatments alone more effective in conservation studies of volcanic tuff stones? (ii) is the emulsion-based or solvent-based application more effective in water-repellent treatments in conservation studies of volcanic tuff stones? Accordingly, the effectiveness of the consolidation and water-repellent treatments was assessed through morphological, physical and mechanical characterization of untreated and treated samples.

Afterwards, the service life of chemical products was determined by applying accelerated weathering tests on both untreated and treated samples. In addition, within the scope of this study, the sustainability of the long-term performance of solvent types used in emulsion-based and solution-based water-repellent products in conservation studies of volcanic tuff stones and their effects on the "green" environment are discussed.

Experimental part

Materials

Volcanic tuff stone (od stone) samples taken from the structure were labelled as AC. These samples were prepared for different experiments which were carried out on the samples to determine chemical composition, mineralogical-petrographic, physical and mechanical properties.

Chemical and petrographic characterization of the stones

Chemical analyses on tuff samples taken from the historical building were carried out with the XRF method using an X-ray spectrometer device in Siemens SRS 3000 and Spectro IQ models. Also, Energy-dispersive X-ray spectroscopy (EDS) was used to define the elemental composition of the samples. The average results of the XRF analysis and EDS analysis of samples are shown in Table 1.

Table 1. Chemical composition of AC samples (XRF and EDS analysis results)

Analysis Method	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	K ₂ O (%)	Na ₂ O (%)	SO ₃ (%)
XRF	61.81	12.44	5.94	4.24	2.40	1.61	2.14	-
EDS	58.28±2	14.93±1	5.88±0.9	3.22±0.7	4.75±0.5	2.20±0.9	4.56±0.9	6.19±0.3

Thin sections were prepared for petrographical-mineralogical analyses and X-ray analysis methods on thin sections were performed using the Philips brand PW-1430 model device. As a result of these analyses, it was seen that the tuffs taken from the structure were rhyolitic, rhyodacitic and dacitic type tuffs containing clinoptilolite type zeolite [35]. As a result of alteration, clay minerals called montmorillonite were found in the internal structures of the stone samples (Fig. 1). Furthermore, the main elements in all stone samples are quartz, plagioclase, orthoclase and alkali feldspar.

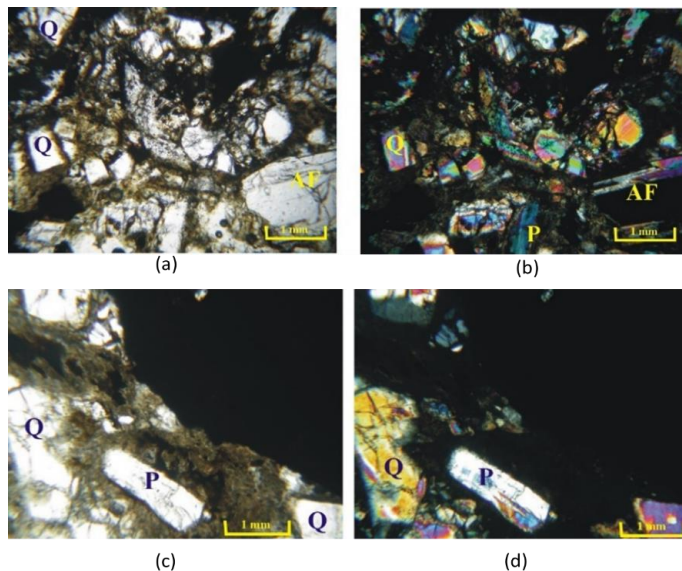


Fig. 1. The intact (a), (b) and deteriorated (c), (d) internal structure of AC; microscope microphotographs under single refractive (a), (c) and under double refractive (b), (d) (Q: quartz, AF: alkali feldspar, P: plagioclase, single refractive: under linear light, double refractive :under parallel light)

The physical and mechanical properties of the stones

Capillary absorption, water absorption under atmospheric pressure, water vapour permeability and specific mass tests were performed on tuff samples taken from the historical building. The values of other physical properties (capillary absorption coefficient, water absorption by weight, water absorption by volume, specific gravity, bulk unit weight, porosity) were calculated according to the results. During the physical property tests, six samples were prepared for each experimental group. The average results of physical property tests of od stone samples are shown in Table 2.

Table 2. The average results of physical property tests of Od stone samples

Samples	N (g/m ² √min.)	Sk (%)	Sh (%)	dh (g/cm ³)	do (g/cm ³)	p (%)
AC	269,8±7,0	7,8±0,005	15,7±0,009	2,05±0,01	2,45±0,02	16±0,005

N: Capillarity absorption coefficient, Sk: water absorption by weight, Sh: water absorption by volume, dh: bulk unit weight, do: specific gravity, p: porozite

The average values of physical properties of AC code samples, water absorption by weight 7-8%, water absorption by volume 15-16%, the bulk unit weight 2.05g/cm³, specific gravity 2.45-2.50g/cm³, porosity rate of 16-18% and water vapour diffusion resistance factor was calculated as 50-60μ (Table 2).

In order to determine the mechanical properties, flexural tensile strength tests were performed on prismatic samples. Secondly, compressive strength tests were conducted on the broken parts after the flexural tensile strength tests. In addition, compressive strength tests were carried out on cube samples of approximately 50x50x50mm. The average results of mechanical property tests are given in Table 3.

Table 3. The average results of mechanical property tests of Od stone samples

Samples	Flexural Tensile Strength (MPa)	Compressive Strength of broken parts in flexural strength (MPa)	Cube Compressive Strength (MPa)	Ultrasonic Pulse Velocity (km/sn)	Dynamic Modulus of Elasticity (MPa)
AC	6,8±0,4	40±2,0	37±2,0	2,49±0,1	15,2 x10 ³

The average values of mechanical properties of AC code samples, flexural tensile strength 5–10MPa, compressive strength of parts broken as a result of flexural tensile strength test 40–45MPa, cube compressive strength 35–40MPa, ultrasonic pulse velocity 2.20–2.70km/sec, the dynamic modulus of elasticity is 12.1–19 x10³MPa.

Methods*Determination of chemical treatment application procedure*

In stone samples, ethyl silicate consolidation product (labelled as TEOS), solution type (diluted with organic solvent) water repellent product (labelled as WR1) and emulsion type water repellent (ethoxy siloxane) product (labelled as WR2) were used. The samples were prepared in three groups. The first group was prepared as untreated reference samples, the second group as the samples treated with a consolidant product (TEOS) followed by application of water-repellent chemical product and the third group treated with only water-repellent chemical products (Fig. 2).



Fig. 2. Application of Chemical Treatments in the Laboratory

The labelling system of the samples used in conservation studies is shown in Table 4. The consolidant product with the TEOS code was undiluted, while the protective water-repellent products were diluted. The general properties of consolidant and water-repellent chemical products are given in Table 5.

In the first treatment, a consolidant and water-repellent product was used. First, the consolidation product TEOS was applied to the sample surfaces with a brush without dilution. TEOS was applied to all six surfaces of the samples in two cycles; after waiting for fifteen minutes, it was used again in two cycles. Then, after fifteen minutes, another application was made in the form of the final two cycles. The process is finished when it is seen that the samples no longer absorb the chemical product. The application period lasted 36-40 minutes. The consolidant product consumption amount is 0.97kg/m^2 . After treatment with the consolidant product, the samples were kept in the laboratory environment (20°C and $50\% \text{RH}$) for two weeks. Then, at the end of the second week, the water-repellent products (WR1 and WR2) were applied separately for two cycles. Then after waiting for fifteen minutes, the process was finished by applying two cycles again.

The water-repellent product alone was applied to the samples in the second treatment. WR1 was diluted with white spirit at a ratio of 1:11 with a brush and WR2 was diluted with water at a ratio of 1:11 with a brush and applied to the six surfaces of the samples in two cycles. After waiting for fifteen minutes, it was applied again in two cycles. Then, after fifteen minutes, another application was made in the form of the final two cycles. The process is finished when it is seen that the samples no longer absorb the chemical product. These samples were kept in the laboratory environment (20°C and $50\% \text{RH}$) for four weeks. Table 6 shows the consumption rates and amounts of all chemical applications made on AC samples.

Table 4. Labelling system of samples used in conservation studies

Labelled Name of Samples	Instructions
AC-UNTR	The reference samples of the tuff stone (od stone) were taken from the historical building, where no chemical product was applied
AC-TEOS+WR1	Samples treated with a consolidant and solution type (diluted with solvent) water-repellent product
AC-TEOS+WR2	Samples treated with a consolidant and emulsion type water-repellent (ethoxy-siloxane) product
AC-WR1	Samples treated with solution type (diluted with solvent) water repellent (methoxy-siloxane) product
AC-WR2	Samples treated with emulsion type water-repellent (ethoxy-siloxane) product

Table 5. General characteristics of chemical products [36-38]

Products	Property	Value	Inspection Method
Consolidant Product (SILRES® BS OH 100) [36]	Density at 25 °C	approx. 0.97 g/cm ³	DIN 51757
	Ignition temperature (liquids)	> 400 °C	DIN 51794
	Flash point	195 °C	ISO 2719
	Catalyst	neutral	-
	Colour	colourless to yellowish	-
Ethyl Silicate Pure Silicic Acid Ester	Ethyl silicate content	approx. 100 wt. %	-
	Water Repellent Product (SILRES® BS 290) [37]	Appearance	colourless, hazy
Mixture of Silane and Siloxane Methyl-octyl methoxysiloxane	Silane-/Siloxane content	approx. 100 wt. %	-
	Density at 25 °C	0.95 - 0.97 g/cm ³	DIN 51757
Water Repellent Product (SILRES® BS SMK 1311) [38]	Viscosity, dynamic at 25 °C	1 - 10 mPa·s	DIN 51562
	Appearance	clear	-
Mixture of Silane and Siloxane (microemulsion concentrate) Methyl-octyl ethoxysiloxane	Colour	yellowish to reddish	-
	Flash point	25 °C	not specified
	Silane-/Siloxane content	100 wt. %	-

Table 6. Consumption rates and amounts of all chemical applications made on AC samples

Measured Criteria	Consolidant		Water Repellents	
	TEOS	WR1	WR2	
Consumption amount (kg/m ²)	0,97	0,89	0,86	
Application time	36 min	36 min	36 min	
Method of Application	2 rounds practice 15 min wait 2 rounds practice 15 min wait 2 rounds practice	2 rounds practice 15 min wait 2 rounds practice 15 min wait 2 rounds practice	2 rounds practice 15 min wait 2 rounds practice 15 min wait 2 rounds practice	
Solvent	without dilution	White spirit (dilution 1:1 by weight)	Demineralized water (dilution 1:1 by weight)	
Environment T°/RH (%)	20°C/50	20°C/60	20°C/60	

Experimental processes and evaluation of the performance of protective products

The experimental process consists of three stages: (i) Determination of macro and microstructure of volcanic tuff samples taken from intact and deteriorated parts of the historical building, (ii) investigation of the effectiveness of chemical treatments on samples taken from historical buildings by experiments, (iii) determining the effectiveness of chemical treatments on the durability properties of aged stones. Durability tests were conducted on deteriorated stones to determine whether the treatments provided benefit the conservation of historical stones and thus their long-term performance was determined. Figure 3 shows the flow chart of the experimental processes applied to the stones.

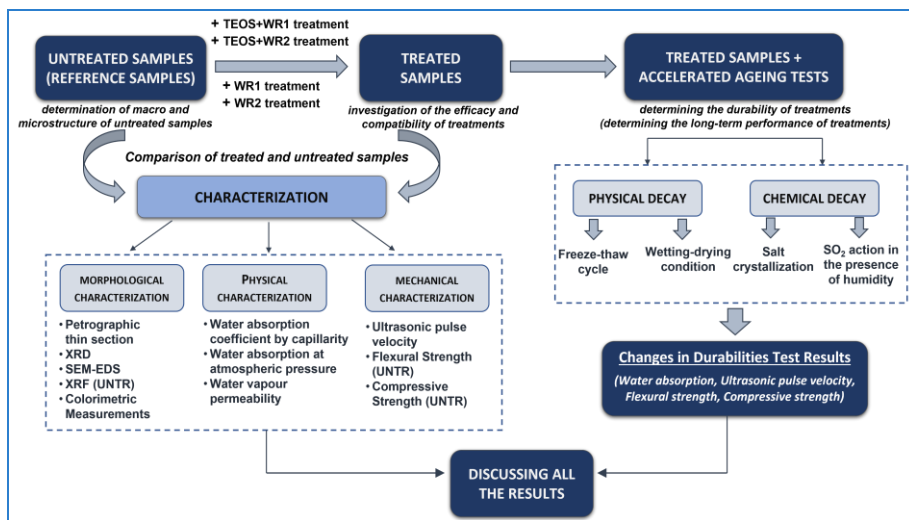


Fig. 3. Flow Chart of Experimental Processes Applied to Stones

Morphological characterization

The morphological characterization of untreated and treated tuffs was carried out by Scanning electron microscopy coupled with energy-dispersive X-ray microanalysis (SEM-EDS) to evaluate the distribution of water-repellent products following the consolidation product in the tuff substrate. SEM micrographs were obtained using a Rigaku RINT 1000 Scanning Electron Microscope, working at 40kV acceleration voltage and 30mA, coupled with energy-dispersive X-ray spectroscopy. All analyzes were performed at a scanning speed of 5 degrees per minute between 3-60° 2θ.

Colorimetric measurements

One month after the treatments, colour measurements were made on the tuff stones when the polymerization period of the protective products was completed. The chromatic variations after colorimetric tests verified treatments according to UNI EN 15886 Standard [39] and using a CM-2600d Konica Minolta spectrophotometer. Chromatic parameters were expressed according to the CIE (Commission Internationale d’Eclairage) L*a*b* space, where a* is the red/green coordinate, b* is the yellow/blue coordinate and L* is the lightness/darkness coordinate [40]. The chromatic change ΔE was calculated according to the following formula:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \tag{1}$$

Physical properties measurement

The water absorption by capillarity coefficient test was applied according to the European Standard UNI EN 15801 [41]. The samples were dried at a constant mass of 105°C.

The samples were immersed in water at a depth of 3-4mm without being moved until the end of the test. The stopwatch device started and at time intervals, the samples were removed from the water and weighed.

The amount of water absorbed per surface unit as a function of time was calculated with this formula:

$$N = [Q / A \cdot \sqrt{t}] \quad (2)$$

where: N is the capillarity coefficient of the stones ($\text{g}/\text{m}^2\sqrt{\text{min}}$), Q is the amount of water per unit time (g), A area of the side immersed in water (m^2) and t times (min).

Turkish Standard TS EN 13755 [42] test method was used to determine the water absorption rate at atmospheric pressure. The samples were dried in the oven to a constant mass and placed in a container after cooling in the desiccator. Water at $20 \pm 5^\circ\text{C}$ was added to up to a quarter of the samples and waited for one hour. Then, half and three-quarters of the samples were kept in water at intervals of one hour and 1.2-2.0cm of water was poured over the samples and they were kept in water and then weighed. After this process, the samples in water were weighed on the balance and the water absorption rates by weight and volume were calculated.

$$\text{Water absorption rate by weight: } S_k = [(G_d - G_k) / G_k] \times 100(\%) \quad (3)$$

$$\text{Water absorption rate by volume: } S_h = [(G_d - G_k) / (G_d - G_{ds})] \times 100(\%) \quad (4)$$

In the formula where G_d is the weight of the sample saturated with water (g), G_k is the weight of the dry sample (g) and G_{ds} : The weight of the sample in water (g).

In addition, the samples were wholly immersed in water at 20°C . Weight gains in certain periods were calculated as a percentage and shown by drawing a graph. The same samples were removed from the water and weight losses were determined as percentage in the laboratory environment. The drying rate graph was drawn over time in the same graph, including the water absorption rate [43].

The water vapour permeability properties of the stones were determined according to the dry cup method defined in the DIN 52615 [44] standard. CaCl_2 was used as water-absorbing material in the experiment. The same test was performed on both treated and untreated samples and the weight differences were calculated. This experiment was conducted in a desiccator environment fixed at $20\text{-}23^\circ\text{C}$ and 90-99% RH. The weight changes of the samples were measured at the same time every day. This experiment continued for three months. Water vapour diffusion resistance coefficient (μ) was calculated with the following formula:

$$\text{Water vapour diffusion resistance coefficient } (\mu) = 1/d (\xi_H \times A \times [(P_1 - P_2) / G] - d_H) \quad (5)$$

In the formula where d is the thickness of the sample (m), ξ_H is the water vapour conductivity of the air, A is the area of the sample (m^2), P is the water vapour pressure value (Pascal), G is the amount of water vapour passing through (kg/h) and d_H is the remaining under the sample is the thickness of the air (m),

$$\xi_H = (0,083 / R_B \times T) \times (P_o / P_h) \times (T / 273)^{1.88} \quad (6)$$

In the formula, T is the temperature in $^\circ\text{K}$, P_h is the average air pressure, P_o is the normal atmospheric pressure.

Mechanical properties measurement

An ultrasonic pulse velocity test (UPV) was applied according to Turkish Standard TS EN 14579 [45]. WTW DIGI EG-C2 model electronic device was used to detect ultrasonic pulses. Repeated readings of the transition time (T, μs) were made until a minimum value was

obtained in the sound transmission. Transmissions of the pulse velocity were calculated from the formula: $V_0 = L/T$ where V is the pulse velocity in km/s, L is the length of the sample in mm and t is the time it takes for the length of the pulse to traverse in μ s. In addition, the dynamic modulus of elasticity values was calculated using the ultrasonic pulse velocity found in the stone samples and the density values of the samples.

The formula is:

$$E_u = V_0^2 \times \rho \times 10^3 \text{ (N/mm}^2\text{)} \quad (7)$$

The simple beam bridge method loaded at the midpoint according to the European Standard UNI EN 12372 [46] was used to determine the flexural tensile strength. This study took the distance between the supports as 100 mm. The samples were placed centred on the supports. The flexural tensile strength was calculated using the equation:

$$B_{eg} = 1.5 \times (P_k \times \ell) / b \times h^2, \quad (8)$$

where: P_k is the load at the break in N, ℓ is the distance between the supports in (mm) and (h) and (b) denote the thickness and width of the sample, respectively.

The uniaxial compressive strength test was applied according to the European Standard UNI EN 1926 [47] on the samples divided into two after the flexural tensile strength test. Each half sample was placed between the loading heads of the test press, the load was applied and the maximum load shown by the test press at the moment of breakage was recorded. This value gives the breaking load value (P_k) and the compressive strength was calculated with the following formula:

$$B = P_k / A, \quad (9)$$

where: A is the cross-sectional area of loading in the samples in mm^2 .

Accelerated weathering tests

Accelerated weathering tests such as wetting-drying cycles, freezing-thawing tests, salt crystallization tests and ageing by the sulfur-dioxide action test were performed after conservation studies. Again, water absorption and ultrasonic pulse velocity tests were performed on the samples that came out of the ageing tests without damage. Accordingly, the treatment efficiency indexes (TEI, %) and performance losses of the chemical applications were evaluated.

A wetting-drying cycle durability test was performed according to ASTM D5313 [48] standard. The treated and untreated samples were dried in distilled water at 20°C for 24 hours and dried in an oven at 60°C for 18 hours and the weight change in certain periods was calculated. The experiment lasted three months.

Freezing-thawing test was applied by keeping the treated and untreated samples in distilled water at 20°C for 6 hours. Then keeping them in a freezer at 22°C for 18 hours. The experiments were carried out in cycles lasting 28 days. The Turkish Standard TS EN 12371 [49] was used in the experiments. Weight changes (%) of the samples in certain periods during the freezing-thawing cycles were calculated.

The salt crystallization test aims to determine the resistance of stone samples to salt attack. In the experiment, treated and untreated samples were first immersed in 14% Na_2SO_4 solution for 6 hours. Secondly, it was kept in an oven at 60°C for 16 hours and then cooled at room temperature for 2 hours. At the end of 20 cycles, the samples were kept in distilled water for one day and after washing them in tap water, they were dried in an oven and weighed. Turkish Standard TS EN 12370 [50] was used in the experiment. The samples' weight changes (%) at certain periods during the experiment were calculated.

Ageing with the sulfur dioxide action test is a method used to evaluate the resistance of stone samples to damage caused by extreme environmental conditions in the presence of

polluting gases. The test was carried out according to the Turkish Standard TS EN 13919 [51]. Stone samples were saturated with water for 24 hours before starting the experiment. The weights of the saturated samples and the samples in water were weighed and then the test was applied. In the test, treated and untreated stone samples were immersion in two different concentrations of H_2SO_3 solutions containing 5% SO_2 in different desiccators for 21 days in a closed container.

The efficacy of the treatment was calculated as a percentage with the treatment efficacy index (TEI) with the following formula:

$$TEI = [W_{tr} - W_{untr} / W_{untr}] \times 100, \quad (10)$$

where: W_{tr} is the physical value treated after treatment; W_{untr} is the first untreated physical value before treatment.

Results and discussion

Morphological characterization

Preliminary experiments were carried out on od stones (volcanic tuff stones) to understand the penetration depths of chemical products. A harmless red dye was added to the consolidant and water-repellent chemical products used and applied to the stones and the penetration depth (by making it visible) was measured. As a result, the penetration depth of the TEOS consolidant product was 3-5mm, the penetration depths of the WR1 water-repellent product diluted with solvent and the WR2 water-repellent product diluted with water were measured between 2-3 mm and no colour change was observed in the stones (Fig. 4).

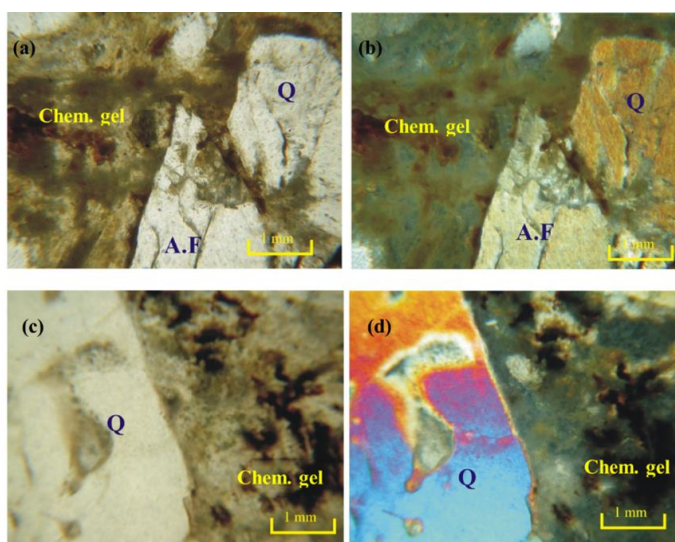


Fig. 4. The chemical gel formed in AC-TEOS+WR1 (a),(b) and AC-TEOS+WR2 (c), (d) microscope microphotographs under single refractive (a),(c) and under double refractive (b),(d)

Thin section analyses were performed on the chemically treated stone samples labelled AC-TEOS+WR1 and AC-TEOS+WR2 to investigate the effect of the treatments on the microstructure. The thin section analysis conducted after AC-TEOS+WR1 application shows silicate gel in a bright image on the matrix between phenocrysts. It has surrounded the crystal edges, especially at alkali feldspar and plagioclase boundaries.

In the thin section analysis after AC-TEOS+WR2 application, silica gels are generally seen on the matrix. Quartz and plagioclase, which should be seen in whiter light tones in Polarized Light Microscope microphotographs under single refractive, are opaquer due to the gel formed after chemical treatments. Also, their optical relief appears to be higher due to silica gel, while plagioclase should be lower (Fig. 4).

In the microscope images of thin-section analyses, it was seen that the chemical silica gel formed in the inner structure of the stone covers the minerals or surrounds the cavities of the minerals (Fig. 4). For this reason, X-ray spectroscopy and scanning electron microscopy analyses were also performed and the results were compared since the colours of the minerals themselves could not be understood in some samples (Fig. 5).

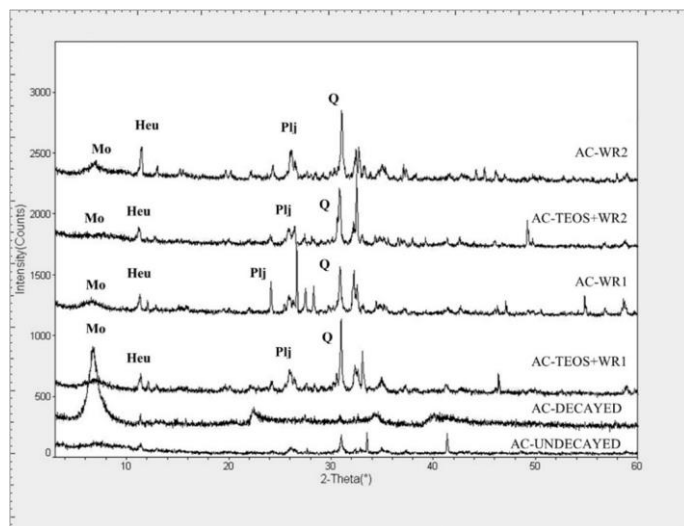


Fig. 5. X-ray Spectroscopy Graphs of AC Samples

Clays and zeolites cannot be seen clearly in thin section analysis regarding crystal morphology, but the presence of clay and zeolite has been detected in the matrix (X-ray diffraction (XRD)) analyses. While the matrix was more greyish brown in the untreated samples, differences were observed in the clayey zeolite matrix in the treated samples.

In the X-ray analysis performed on the treated and untreated samples, the Montmorillonite mineral peak, which is the alteration product, decreased and the increase in the SiO₂ (silica) mineral peak became quite evident in the chemically applied samples (Fig. 5). The order of succession of the chemical treatments, respectively, is as follows: the best results were obtained from the samples applied TEOS+WR1 followed by WR1, TEOS+WR2 and WR2. Essential minerals are shown in these charts.

SEM micrographs of tuff stone (od stone) samples applied TEOS+WR1, TEOS+WR2, WR1 and WR2 chemical products were taken (Figs. 6 and 7). In SEM micrographs of untreated tuff samples, od stone has a loose textured microstructure with capillary cracks in places and therefore exhibits heterogeneous behaviour (Fig. 8).

However, SEM micrographs of treated stone samples (especially 2000x-3500x) show a layer of silica gel homogeneously enveloping the stone matrix as a cover. In the EDS (Energy Dispersive Spectrum) analysis results, the SiO₂ ratio, respectively 65–75% in untreated samples, 80–100% in TEOS+WR1 treated samples and around 90% in TEOS+WR2 treated samples (Figure 6, Figure 7). The SiO₂ ratio was around 70-80% in the samples treated with the water-repellent product alone. Figure 7 shows SEM micrographs of tuff samples treated with water-repellent (WR1-WR2) products alone.

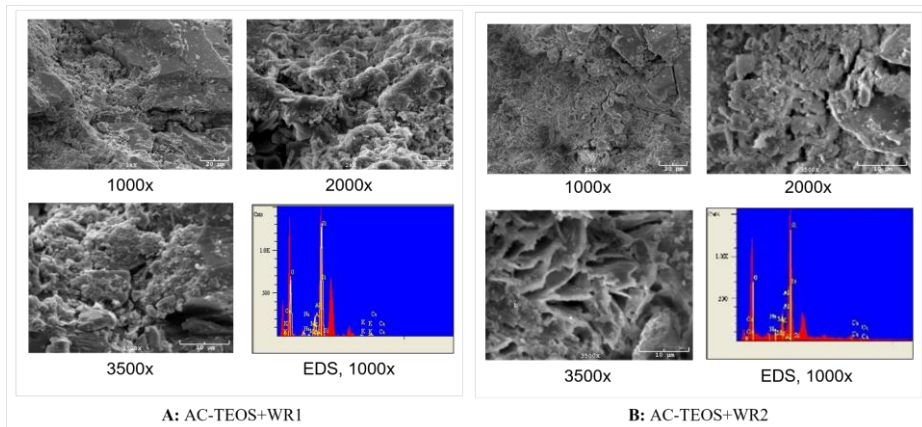


Fig. 6. SEM-EDS Analysis of AC-TEOS+WR1 (A) and AC-TEOS+WR2 (B) Stone Samples

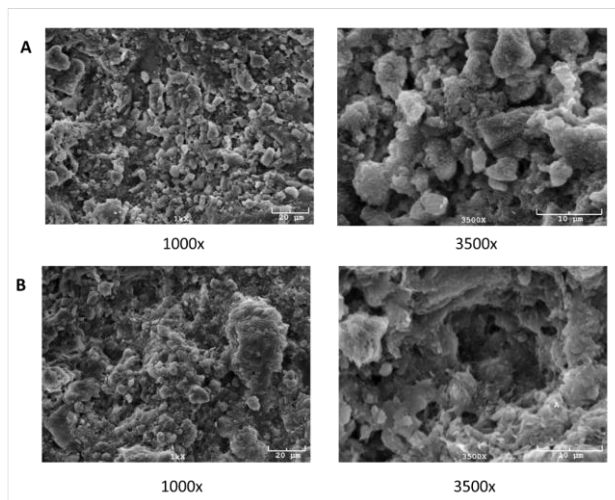


Fig. 7. SEM Analysis of AC-WR1 (A) and AC-WR2 (B) Stone Samples

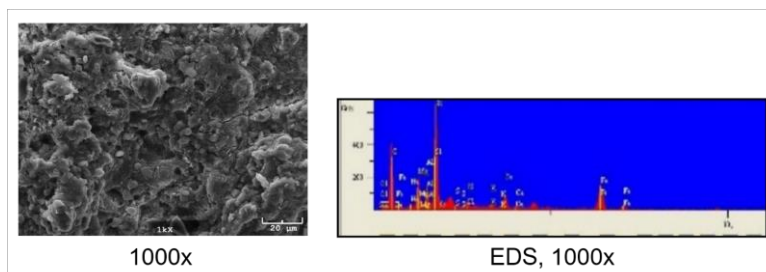


Fig. 8. SEM-EDS Analysis of Untreated Samples of AC Stone Sample

Colorimetric Measurements

In the field of stone preservation, there are no absolute rules for the interpretation of colour changes. Based on visual observations and measurements, different authors propose different values (from 1 to 5) as the threshold for acceptable colour change. After all treatments, all colour variation values are within the acceptable limits (ΔE^* value < 5) [52, 53]. All treatments showed a lower colour variation (ΔE^*) than 3, thus confirming the suitability of all

treatments for restoring and conserving purposes. However, all treatments with negative ΔL^* values result in minimal darkening of the tuff samples. Therefore, in treatments using solution-typed water-repellent products (AC-TEOS+WR1 and AC-WR1), the solvent may have caused slight darkening of the tuff stones. The obtained values are reported in Table 7.

Table 7. Color measurements in treated stone samples

Treatments	Δ (Treated and untreated samples)			
	ΔL^*	Δa^*	Δb^*	ΔE^*
AC-TEOS+WR1	-1.93	-0.88	1.12	2.40
AC-TEOS+WR2	-0.87	0.39	0.63	1.14
AC-WR1	-0.93	-0.42	0.75	1.27
AC-WR2	0.41	0.17	0.31	0.54

The results of physical property tests

The physical property test results repeated on the same samples before and after chemical treatment are given in Table 8 comparatively.

In order to interpret the changes in the movement of liquid and gaseous water in the pores of the stone, the calculation of total water absorption, capillarity absorption coefficient, drying rate and water vapour diffusion resistance factor gives a more realistic evaluation opportunity. The water absorption and drying rates calculated as a result of the experiments performed on the treated and untreated AC samples are shown graphically in figure 9. When these results were compared, it was determined that the water absorption and drying rate of AC-TEOS+WR1 and AC-WR1 samples, respectively, after chemical applications were lower than AC-TEOS+WR2 and AC-WR2 samples.

The values in Table 8 and the graphs in figure 9 were used to calculate the decrease rates in the capillary water absorption values of the samples, the water absorption values of the samples and the increasing rates of the bulk unit weight of the samples. The values of chemical treatment efficiency indexes are shown in figure 10.

Table 8. The Effect of Chemicals on Physical Properties of Stone Samples

Applications	Initial N ($g/m^2\sqrt{min.}$)	Initial Sk (%)	Initial Sh (%)	Initial dh (g/cm^3)	Final N ($g/m^2\sqrt{min.}$)	Final Sk (%)	Final Sh (%)	Final dh (g/cm^3)
AC-TEOS+WR1	308,4 ±5,0	8,0 ±0,001	17,03 ±0,01	2,14 ±0,005	25,94 ±4,0	1,2 ±0,001	2,65 ±0,002	2,17 ±0,01
AC-TEOS+WR2	270,83 ±5,0	8,1 ±0,002	17,63 ±0,07	2,15 ±0,01	34,3 ±4,0	1,6 ±0,003	3,49 ±0,02	2,18 ±0,001
AC-WR1	303,1 ±5,0	8,0 ±0,001	17,2 ±0,002	2,13 ±0,005	29,5 ±2,0	1,2 ±0,001	2,6 ±0,002	2,15 ±0,003
AC-WR2	285,3 ±5,0	7,9 ±0,008	16,91 ±0,09	2,12 ±0,05	33,16 ±2,0	2,5 ±0,003	5,4 ±0,005	2,13 ±0,05

N: Capillarity absorption coefficient, Sk:water absorption by weight, Sh:water absorption by volume, dh:bulk unit weight

After chemical treatment, capillary water absorption rates decreased by 91% for the AC-TEOS+WR1 sample, 90% for the AC-WR1 sample, 89% for the AC-TEOS+WR2 sample and 88% for the AC-WR2 sample, respectively. In addition, water absorption rates after chemical treatment decreased by 85% in the AC-TEOS+WR1 sample, 84% in the AC-WR1 sample, 82% in the AC-TEOS+WR2 sample and 70% in the AC-WR2 sample, respectively (Fig. 10). These results are similar to the graphs in figure 9. In addition, the bulk unit weight of the stones increased by approximately 1.4% after the treatments labelled AC-TEOS+WR1 and AC-

TEOS+WR2, in which the consolidant and water-repellent products were applied together. After the treatments labelled AC-WR1 and AC-WR2, only water-repellent product treatments, the bulk unit weight of the stones increased by approximately 1% (Fig. 10). In general, it is understood that after chemical treatment, silane-siloxane-based products increase the bulk unit weight of the stone by 1–1.5% and decrease the capillary water absorption and water absorption values by 80–90%.

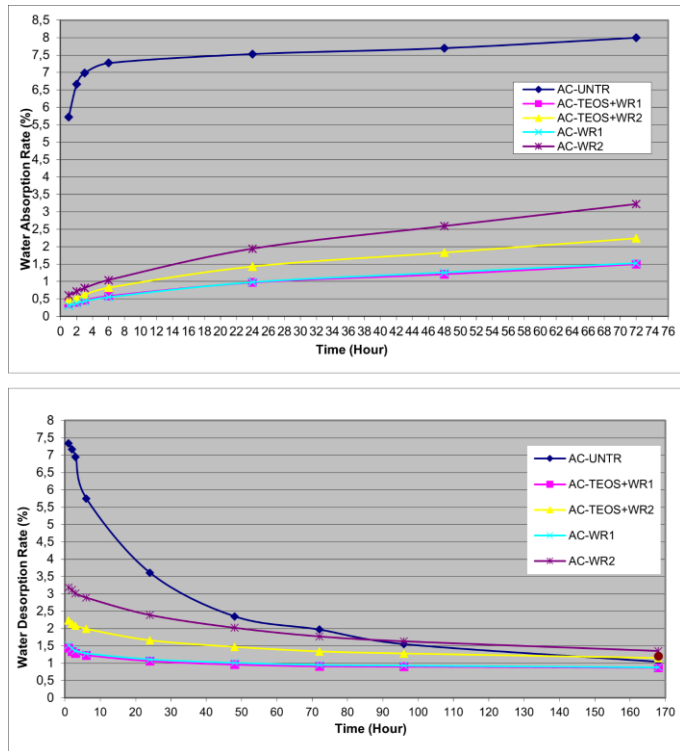


Fig. 9. Effect of Chemicals Materials on Water Absorption Rate of AC Samples and Water Desorption Rate of AC Samples

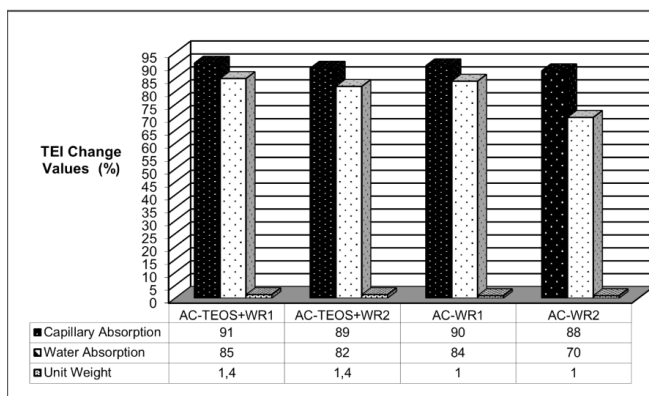


Fig. 10. Treatments Efficiency Indexes on Physical Characterizations of AC Samples

The water vapour diffusion resistance factor test was carried out by weighing the weights of the same samples in the same temperature and humidity environment before and after the chemical treatment was applied to the AC samples. The experimental results were calculated comparatively and the chemical treatment efficiency index (TEI) was calculated (Table 9).

Table 9. Water vapour diffusion resistance coefficients and TEI values of AC samples

Applications	Samples	Water vapour diffusion resistance coefficient before chemical treatment	Water vapour diffusion resistance coefficient after chemical treatment	Water vapour diffusion resistance coefficient TEI values (%)
TEOS+WR1	1AC1	60	70	TEOS+WR1 % 12
TEOS+WR1	1AC2	54	60	
TEOS+WR1	1AC3	59	64	
AVERAGE		58±6,0	65± 7,0	
TEOS+WR2	2AC1	55	58	TEOS+WR2 % 11,5
TEOS+WR2	2AC2	50	55	
TEOS+WR2	2AC3	53	62	
AVERAGE		52±2,0	58±3,0	
WR1	3AC1	50	55	WR1 % 8
WR1	3AC2	46	48	
WR1	3AC3	50	53	
AVERAGE		48±2,0	52±3,0	
WR2	4AC1	61	68	WR2 % 8
WR2	4AC2	58	60	
WR2	4AC3	60	66	
AVERAGE		60±1,0	65±4,0	

After chemical treatments, the water vapour diffusion resistance factor increased by 12% in the AC-TEOS+WR1 sample, 11.5% in the AC-TEOS+WR1 sample and 8% in the AC-WR1 and AC-WR2 samples, respectively. It is accepted that the chemical materials used in consolidation and conservation studies increase the original stone's water vapour diffusion resistance factor by 10-15% at most [54]. Thus, the experimental results are at an acceptable level.

The results of mechanical property tests

Ultrasonic pulse velocity test was performed on six chemically treated and untreated AC samples and the results were compared. The ultrasonic pulse velocity in the chemically treated samples increased by about 30% compared to the untreated samples. In another study, while the treatment efficiency index (TEI) value of ultrasonic pulse velocity was found to be 30% in the samples with the consolidant and water-repellent application, it was found to be at most 15% in the samples using water-repellent alone [55]. Similar results to these results were obtained in this study as well and are shown in figure 11.

It is expected that the ultrasonic pulse velocity increase in the samples where the consolidant and water-repellent products are applied together is higher than in the samples in which the other water-repellent product is applied alone. Because while the weight of the samples treated with more than one chemical product increases, the pore filling also increases.

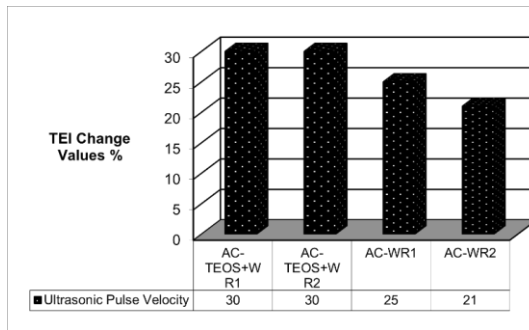


Fig. 11. The treatments Efficiency Indexes on Ultrasonic Pulse Velocity of AC Samples

The results of accelerated weathering tests

In this study, some accelerated weathering tests, also recommended in the ASTM E-2167 [15] standard, were carried out to determine preservation treatments' durability (long-term performance) and service life. These are accelerated ageing tests such as wetting-drying cycles, freezing-thawing tests, salt crystallization tests and ageing by the sulfur-dioxide action test [15]. These experiments were performed at 30 cycles to compare the results. In order to compare the durability of the treated and untreated samples and chemical materials, the water absorption and ultrasonic pulse velocity tests were repeated on the samples that did not deteriorate in the ageing tests and the change in the chemical treatment efficiency index was calculated. After 30 cycles of the wetting-drying cycles test, the physical and mechanical property tests were repeated on the same samples and the chemical treatment efficiency indexes (TEI) were calculated. These values are shown comparatively in figure 12. The TEI change rates in the physical properties of the samples were calculated by taking the differences in the treatment efficacy index values found before and after the wetting-drying cycle test. In calculating the TEI change rates in the samples' mechanical properties (flexural and compressive strength), the flexural and compressive strength values of the chemically untreated (UNTR) samples before the wetting-drying cycle test were taken into account. The values found before the ageing test and the changes in the flexural and compressive strength values found after the ageing test were calculated as percentages and shown in graphs.

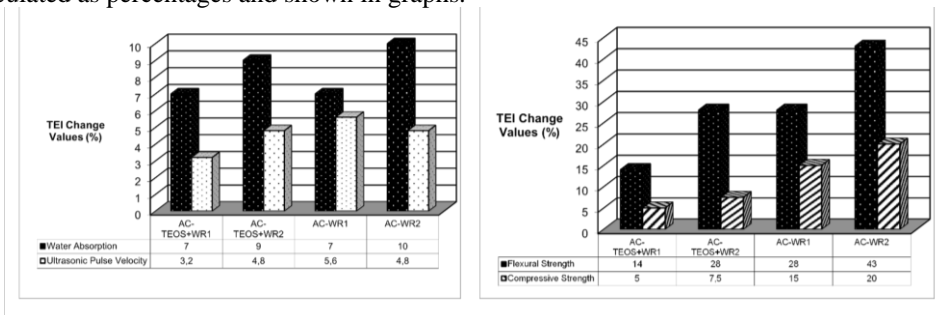


Fig. 12. The Effect of the Wetting-Drying Cycles Tests on the Physical and Mechanical Properties of the Stones (TEI %)

The wetting-drying cycles durability tests were the least damaging of the other accelerated weathering tests. Weight changes during this experiment were not very pronounced. The water absorption ratio of the untreated samples increased by 2.5% in the AC samples at the end of the accelerated weathering test. On the other hand, the changes in the treatment efficacy indexes in the water absorption test of the treated samples were not found to be very different. It has been observed that they maintain their protective properties. Since the treated samples

absorb less water, they were not affected much by the wetting-drying cycle test under normal pressure. The lower percentage of change in the AC samples is explained by the fact that the clay particles formed as a result of alteration in the internal structures of these samples activate during the wetting-drying test and block the significant gaps in the stone pores. Since it does not absorb much water, the total water absorption ratio changes slightly in this case.

At the end of the freezing-thawing durability test, water absorption and ultrasonic pulse velocity tests were performed on the samples before the mechanical tests and the results were compared with the previous values. The change rates in the obtained chemical treatment efficiency indexes (TEI) are given in figure 13 collectively. In addition, after the water absorption and ultrasonic pulse velocity tests, the values obtained by flexural and compressive strength tests were compared with those before the accelerated weathering test. Moreover, decreases in strengths were evaluated as changes in chemical treatment efficiency indexes (TEI) (Fig. 13).

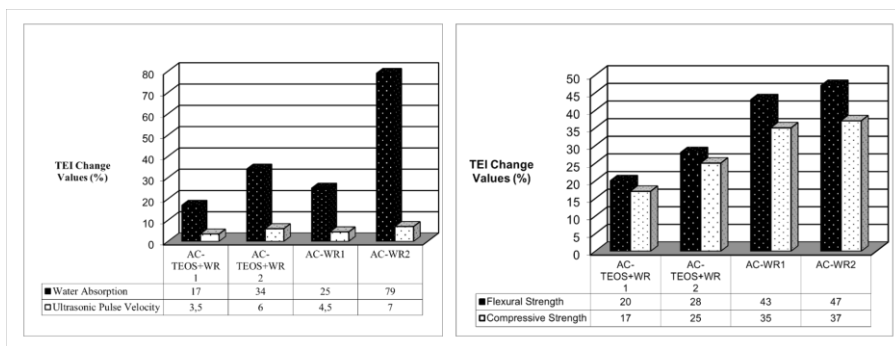


Fig. 13. The Effect of the Freezing-Thawing Cycles Tests on the Physical and Mechanical Properties of the Stones (TEI %)

As a result of accelerated weathering tests, the water absorption rate of the untreated samples increased by about 15%. This increase is more than the increase in the wetting-drying test can be explained by the internal stresses created by the freezing water in the stone. As a result of the freezing-thawing resistance test, the protection properties of the chemically treated samples in the water absorption test changed a lot. The performance (efficiency value) of the chemical materials (products) in the water absorption test decreased by 17% in samples treated with TEOS+WR1, decreased by 34% in samples treated with TEOS+WR2, decreased by 25% in samples treated with WR1 (emulsion type) and decreased by 79% in the sample treated with WR2 (solution type) samples (Fig. 13). The freezing-thawing resistance test was more effective in the samples using an emulsion-type water-repellent product. On the other hand, the treatment type least affected by the freezing-thawing resistance test was the TEOS+WR1 applied samples. Despite the performance reductions, it has been determined that the chemically treated samples are in much better condition than the untreated samples.

As there was no significant change in the water absorption values of the untreated samples due to the wetting-drying and freezing-thawing resistance tests, it was thought that the samples were not affected at all by these tests. However, the ultrasonic pulse velocity values were found to be quite different afterward. The low water absorption of these samples was due to the clay particles displacing and swelling in the water, entering the spaces in the stone pores and blocking the pores. Weight changes are not evident since they dry more slowly than the treated samples.

Salt crystallization resistance tests were performed for a total of 20 cycles. At the end of this test, all untreated AC samples were fragmented on the 15th cycle. The dark brown patches on the surface of the untreated AC samples disintegrated after they were hollowed out. The salt crystallization resistance test was the most destructive ageing test. This result showed that the

crystallization of the salt entering the stone's internal structure causes very large internal stresses in the stone; thus, it is more effective in untreated samples with high water absorption capacity. The most successful results were found in AC-TEOS+WR1, AC-TEOS+WR2 and AC-WR1 samples. The TEI change rates obtained in the results of repeated water absorption, ultrasound velocity and mechanical property tests after the salt crystallization resistance test are shown in figure 14.

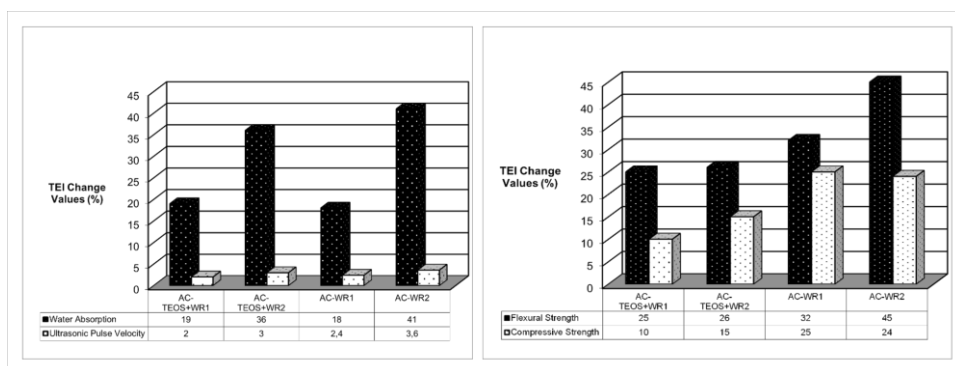


Fig. 14. The Effect of the Salt Crystallization Cycles Tests on the Physical and Mechanical Properties of the Stones (TEI %)

The salt crystallization resistance test was the one that most affected the efficiency values of chemical products. The performance (efficiency value) of chemical materials (products) in the water absorption test decreased by 19% in samples treated with TEOS+WR1, decreased by 36% in samples treated with TEOS+WR2, decreased by 18% in samples treated with WR1 (emulsion type) and decreased by 41% in the sample treated with WR2 (solution type) samples (Fig. 14). After the salt crystallization resistance test, there was almost no difference in the ultrasonic pulse velocity values of the stone samples because this is the result of salts crystallizing and filling the internal structure of the stone samples and the clay movements in the stone pores.

The effects of all accelerated weathering tests on the mechanical properties of the untreated reference samples are shown in Table 10. These values were compared with the mechanical property values of the untreated samples before the experiments and were calculated as percentages of loss of performance changes.

As a result of accelerated weathering tests, the mechanical properties of the treated and untreated stone samples were compared. As shown in Table 10, as a result of the wetting-drying cycles test of the untreated samples, the flexural strength loss was 40%, the compressive strength loss was 25% and as a result of the freezing-thawing cycles test, the flexural strength loss was 52%, while the compressive strength loss was 40%. As a result of the salt crystallization resistance test, the untreated samples were destroyed with the greatest damage.

Table 10. Effects of Ageing Tests on the Mechanical Properties of the Untreated Sample

Decrease Rates in Mechanical Properties	Ultrasonic Pulse Velocity Loss, (%)	Flexural Strength Loss, (%)	Compressive Strength Loss, (%)
End of wetting-drying cycles tests AC- UNTR	9,5	40	25
End of freezing-thawing cycles tests AC- UNTR	14	52	40
End of salt crystallization cycles tests AC- UNTR	they completely disintegrated.		

Moreover, as a result of accelerated weathering tests, chemical treatments generally improved the mechanical properties of the stones. In particular, the mechanical strengths of the samples treated with TEOS+WR1 and TEOS+WR2 (applications together with a consolidant and a water-repellent) are better than those treated with WR1 and WR2 (only water-repellent applications) (Figs. 12-14). The AC-TEOS+WR1 sample provided the best flexural and compressive strength against wetting-drying, freezing-thawing and salt effects crystallization.

Conclusions

Conservation studies were carried out on volcanic tuff stone samples (od stone samples) taken from a historical building. The degraded stones taken from the building were treated with both solventless mixtures of ethyl silicates (TEOS) tetraethoxysilane consolidation product followed by applying two different silane-siloxane-based water-repellent commercial products and only two different silane-siloxane based water repellent commercial products (one emulsion and the other solution based). The effects of using various chemical products were investigated in the study and their durability properties were examined. In addition, the sustainability of emulsion and solution-type solvent materials in water-repellent products on the long-term performance of preservation treatments and environmental effects are discussed.

As a general result of the conservation studies, TEOS+WR1 application (ethyl silicate followed by silane-siloxane based solution type water repellent) was the most successful treatment in improving the physical properties of the stones and preserving the performance of the treated stones as a result of accelerated weathering tests. In general, samples treated with all consolidant products followed by water-repellent products (AC-TEOS+WR1 ve AC-TEOS+WR2) were more successful in improving the physical properties of tuff stones than samples treated with water-repellent products (AC-WR1 ve AC-WR2). However, when the sustainability of their performance in accelerated weathering tests was examined, the most successful result was obtained in the samples treated with TEOS+WR1, followed by the second most successful results in the samples treated with WR1 alone. In this case, according to the performance order, TEOS+WR1, WR1 and TEOS+WR2 applications were found to be successful, respectively. The most significant loss of performance was in the samples treated with WR2. As a result, consolidant and solvent-based water-repellent products fill some of the macro-voids in the stones, providing better penetration and adapting to the internal silicate structure. Thus, applications treated with a consolidant followed by a water-repellent product succeeded in all experiments as they were less affected by water, moisture and salt.

The results obtained by the colorimetric measurements showed that all products did not cause any significant variations in original colour after treatment and negligible colour variations were observed, i.e., all values are within an acceptable limit ($\Delta E^* < 3$). Although the TEOS+WR1 treatment showed the best consolidation and water-repellency performance in tuff stones, it caused more colour change ($\Delta E^* = 2.40$) than other treatments. This may have been caused by the fact that it was a solvent-based water-repellent product. The colour change was less in treatments with emulsion-type water-based water-repellent products (TEOS+WR2 and WR2). This result shows that water-based products are generally more suitable for stone preservation treatments in terms of colour.

Solvent-based water-repellent materials may show different performances depending on their polymerization degree. In this study, it was understood that emulsion-type water-repellent applications were significantly affected by the moisture content of the stone. Conservation studies with water-repellent materials vary depending on the structure and properties of the stones. Especially in volcanic tuff stones, the penetration depth problems of chemicals arise due to different types of clay. For this reason, it is considered that more success can be achieved when solvent-based water-repellent products are used after ethyl silicate consolidation application in such stones.

However, consideration should be given to whether a solvent-based material is necessary to minimize toxicity without compromising the efficacy of stone preservation treatments and simultaneously increase the sustainability of a treatment process. If a solvent is required, consider how much surface protective materials and solvent are needed, how long it will be used and which type will be the most environmentally friendly. However, it can be challenging to determine this based solely on an individual's knowledge and experience. Other evaluation sources should be sought, such as case studies and various published guidelines [56].

Preservation-protection-repair studies are required for detailed studies on tuff stones, which have a very different structure than stones such as limestone and sandstone. The working systematics set out at the end of this study should be followed for each tuff stone. However, testing their suitability in the laboratory environment is recommended before deciding on the selection and application methods of the products applied in conservation studies. Because the success of preservation applications depends primarily on the type of stone, then the kind of products, application technique, penetration ability and durability.

Acknowledgments

The authors thank Prof.Dr. Erol GÜRDAL for the invaluable advice.

References

- [1] M.S. Todorović, O. Ećim-Đurić, S. Nikolić, S. Ristić, S. Polić-Radovanović, *Historic building's holistic and sustainable deep energy refurbishment via BPS, energy efficiency and renewable energy-A case study*, **Energy Building**, **95**, 2015, pp.130–137.
- [2] Z. Ahunbay, *Karamürsel'in Od Taşı ve Tarihi Yapılarda Kullanımı (Karamürsel's Od Stone and Its Use in Historical Buildings)*, **Uluslararası Kara Mürsel Alp ve Kocaeli Tarihi Sempozyumu II (International Karamürsel Alp and Kocaeli History Symposium II)**, Kocaeli, c. III, 2016, pp. 1797-1806.
- [3] A.Z. Miller, A. Dionisio, L. Laiz, M.F. Macedo, C. Saiz-Jimenez, *The influence of inherent properties of building limestones on their bioreceptivity to phototrophic microorganisms*, **Annals of Microbiology**, **59**, 2009, pp. 705-713.
- [4] C.A. Grissom, *The determination and treatment of volcanic stone: A review of the literature*, **Proceedings of the International Meeting About Lavas and Volcanic Tuffs**, Easter Island, Chile, 1990, pp. 3-10.
- [5] G.G. Amoroso, V. Fassina, **Stone Decay and Conservation: Atmospheric Pollution, Cleaning, Consolidation and Protection**, Elsevier Science Ltd., 1983.
- [6] F. Iucolano, A. Colella, B. Liguori, D. Calcaterra, *Suitability of silica nanoparticles for tuff consolidation*, **Construction and Building Materials**, **202**, 2019, pp. 73-81.
- [7] A.B. Yavuz, *Durability assessment of the Alacatu tuff (Izmir) in western Turkey*, **Environmental Earth Sciences**, **67**(7), 2012, pp. 1909-1925.
- [8] H.R. Sasse, R. Snethlage, *Evaluation of stone consolidation treatments*, **Science and Technology for the Cultural Heritage**, **5**(1), 1996, pp. 85-92.
- [9] E. Hansen, E. Doehne, J. Fidler, J. Larson, B. Martin, M. Matteini, C. Rodriguez-Navarro, E. Sebastian-Pardo, C. Price, A. Tagle, J.M. Teutonico, N. Weiss, *A review of selected inorganic consolidants and protective treatments for porous calcareous materials*, **Reviews in Conservation**, **4**, 2003, pp. 13-25, DOI:10.1179/sic.2003.48.Supplement-1.13
- [10] R. Snethlage, K. Sterflinger, **Stone in Architecture**, Springer, Berlin, Heidelberg, 2011, pp. 411-544.
- [11] G. Wheeler, *Alkoxysilanes and the consolidation of stone*, **Research in Conservation**, Los Angeles, Getty Conservation Institute, 2005.

- [12] E. Doehne, C.A. Price, *Stone Conservation: An Overview of Current Research*, Getty Conservation Institute, Los Angeles, CA, 2011.
- [13] Z.S. Karkas, S. Acun Özgünler, *A Method Suggestion That Can Be Used in Conservation of Masonry Materials in Historical Buildings*, **Süleyman Demirel University Journal of Natural and Applied Sciences**, **25**(3), 2021, pp. 564-571. DOI: 10.19113/sdufenbed.884228.
- [14] * * *, *Interventi conservativi: Progettazione, esecuzione e valutazione preventiva*, **NORMAL 20/85**, Istituto Centrale del Restauro, Rome, 1985.
- [15] * * *, *Standard Guide for Selection and Use of Stone Consolidants*, **ASTM E2167-01**, USA: American Standards Institute, 2008.
- [16] * * *, *Conservation of Cultural Heritage- Surface protection for porous inorganic materials-Laboratory test methods for the evaluation of the performance of water repellent products*, **BS EN 16581**, British Standards Institution, 2014.
- [17] J. Turk, A. Pranjić, A. Hursth, R. Turner, J. Hughes, *Decision support criteria and the development of a decision support tool for the selection of conservation materials for the built cultural heritage*, **Journal of Cultural Heritage**, **37**, 2019, pp. 44-53, DOI:10.1016/j.culher.2018.10.001
- [18] * * *, **Conservation of Cultural Heritage in the Arab Region Issues in the Conservation and Management of Heritage Sites**, International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM), Rome, Italy, 2016.
- [19] Z.S. Karkas, *Tarihi Yapıların Cephelelerinde Kullanılan Kagir Yapı Malzemelerinde Konservasyon Çalışmalarının İrdelemesi ve Sistemik Bir Yöntem Önerisi (Investigation of Conservation Studies in Masonry Building Materials Used on the Facades of Historical Buildings and a Systematic Method Proposal)*, **Master Thesis**, İTÜ Fen Bilimleri Enstitüsü, Yüksek Lisans tezi (İTÜ Institute of Science and Technology, İstanbul, 2020.
- [20] P.L. Bianchetti, G. Lombardi, C. Meucci, *The Study of the Degradation of Tuff Blocks Used in the Roman Temple of Cibele (Rome, Italy)*, **Proceedings of the 4th International Congress on the Deterioration and Preservation of Stone Objects**, Louisville, July 7-9, 1982, pp. 29-38.
- [21] E. De Witte, *Conservation of the Göreme Rock, The Safeguard of the Rock-hewn Churches of the Göreme Valley*, **Proceedings of the International Seminar**, Ürgüp-Capadocia, Turkey, 1993, pp. 109-124.
- [22] B.S. da Fonseca, A.P. Ferreira Pinto, S. Piçarra, M. de Fatimas Montemor, *Challenges of Alkoxysilane-Based Consolidants for Carbonate Stones: From Neat TEOS to Multipurpose Hybrid Nanomaterials*, **Advanced Materials for the Conservation of Stone**, 2018, pp. 185– 207, DOI: 10.1007/978-3-319-72260-3_9.
- [23] D. Chelazzi, R. Camerini, R. Giorgi, P. Baglioni, *Nanomaterials for the Consolidation of Stone Artifacts* **Advanced Materials for the Conservation of Stone**, (Editors: M. Hosseini and I. Karapanagiotis), Springer, Cham, 2018.
- [24] H. De Clercq, S. De Zanche, G. Biscontin, *TEOS and time: the influence of application schedules on the effectiveness of ethyl silicate based Consolidants/Tetraethoxysilan (TEOS)*, **Restoration of Buildings and Monuments** **13**(5), 2007, pp. 305–318, <https://doi.org/10.1515/rbm-2007-6153>
- [25] E.S. Goins, *Alkoxysilane stone consolidants: the effect of the stone substrate upon the polymerization process*, **PhD Thesis**, University College London, 1995, 200p.
- [26] E. Franzoni, G. Graziani, E. Sassoni, *TEOS-based treatments for stone consolidation: acceleration of hydrolysis–condensation reactions by poulticing*, **Journal of Sol-Gel Science and Technology**, **74**(2), 2015, pp. 398–405.
- [27] T. Berto, S. Godts, H. De Clercq, *The effects of commercial ethyl silicate based consolidation products on limestone*, **Science and Art: A Future for Stone Stone: Proceedings of the 13th International Congress on the Deterioration and**

- Conservation of Stone, Volume 1. Paisley: University of the West of Scotland.** (Editors: J. Hughes and T. Howind), 2016, pp. 271–280.
- [28] G. Graziani, E. Sassoni, E. Franzoni, *Consolidation of porous carbonate stones by an innovative phosphate treatment: mechanical strengthening and physical-microstructural compatibility in comparison with TEOS based treatments*, **Heritage Science**, **3**(1), 2015. <https://doi.org/10.1186/s40494-014-0031-0>.
- [29] Y. Liu, J. Liu, *Synthesis of TEOS/PDMS-OH/CTAB composite coating material as a new stone consolidant formulation*, **Construction and Building Materials**, **122**, 2016, pp. 90–94, <https://doi.org/10.1016/j.conbuildmat.2016.06.069>
- [30] M. Meléndez-Zamudio, I. Bravo-Flores, E. Ramírez-Oliva, A. Guerra-Contreras, G. Álvarez-Guzmán, R. Zárraga-Nuñez, A. Villegas, M. Martínez-Rosales, *Cervantes J. An Approach to the Use of Glycol Alkoxysilane-Polysaccharide Hybrids in the Conservation of Historical Building Stones*, **Molecules**, **26**(4), 2021, Article Number 938, <https://doi.org/10.3390/molecules26040938>
- [31] * * *, *Clear Water Repellents for Above Grade Masonry and Horizontal Concrete Treatments*, **SWRI**, Kansas City, ABD, Waterproofing and Restoration Institute, 1994.
- [32] A.E. Charola, *Water repellents and other protective treatments: A critical review*, **Proceedings of the 3 129 rd. International Conference on Surface Technology with Water Repellent Agents**, **Aedificatio Publishers**, 2001, pp. 410.
- [33] H. Kober, F.H. Wittman, A.J.M. Siemes, L.G.W. Verhoef, *Water thinnable silicon impregnating agents for masonry protection*, **Proceedings of the 1 132 th. International Symposium on Surface Treatment of Building Materials with Water Repellent Agents**, Delft, Netherlands, 1995, Article Number:13.
- [34] F.P. Byrne, S. Jin, G. Paggiola, T.H.M. Petchey, J.H. Clark, T.J. Farmer, A.J. Hunt, C.R. McElroy, J. Sherwood, *Tools and Techniques for solvent selection: green solvent selection guides*, **Sustainable Chemical Processes**, **4**(7), 2016, Article Number: 7. <https://doi.org/10.1186/s40508-016-0051-z>.
- [35] S. Acun Özgünler, *Tarihi Yapılarda Kullanılan Volkanik Tüflerin Konservasyonu Üzerine Bir Araştırma: Od Taşı Örneği*, **PhD Thesis**, İTÜ Fen Bilimleri Enstitüsü, İstanbul, 2007.
- [36] * * *, **SILRES® BS OH 100**. <https://www.wacker.com/h/en-us/silanes-siloxanes-silicates/ethyl-silicates/silres-bs-oh-100/p/000008022> [accessed 30.05.2022].
- [37] * * *, **SILRES® BS 290**. <https://www.wacker.com/h/en-us/silanes-siloxanes-silicates/silres-bs-290/p/000010606> [accessed 30.05.2022]/
- [38] * * *, **SILRES® BS SMK 1311**. <https://www.wacker.com/h/en-us/silanes-siloxanes-silicates/silane-siloxane-mixtures/silres-bs-smk-1311/p/000010621> [accessed 30.05.2022].
- [39] * * *, *Conservation of cultural property - Test methods - Colour measurement of surfaces*, **UNI EN 15886**, Ente Nazionale Italiano di Unificazione (Italian National Unification), 2010.
- [40] * * *, *Colorimetry. CIE 1976 L*a*b* Color space*, **EN ISO 11664-4**, Ente Nazionale Italiano di Unificazione (Italian National Unification), 2011.
- [41] * * *, *Conservation of cultural property. Test methods. Determination of water absorption by capillarity*, **BS EN 15801**, British Standards Institution, London, United Kingdom, 2009.
- [42] * * *, *Natural stone test methods—Determination of water absorption at atmospheric pressure*, **TS EN 13755**, Turkish Standard Institution, Ankara, Turkey, 2009.
- [43] E. Borelli, A. Urland, **Laboratory Handbook: Conservation of Architectural Heritage, Historic Structures and Materials**, ICCROM-UNESCO-WHC, ARC, Roma, 1999.
- [44] * * *, *Testing of thermal insulating materials; determination of water vapour (moisture) permeability of construction and insulating materials*, **DIN 52615**, German Institute for Standardization, Germany, 1987.

- [45] * * *, *Natural stone test methods—Determination of sound speed propagation*, **TS EN 14579**, Turkish Standard Institution, Ankara, Turkey, 2006.
- [46] * * *, *Natural Stone Test Methods - Determination of Flexural Strength Under Concentrated Load*, **UNI EN 12372**, Ente Nazionale Italiano di Unificazione (Italian National Unification), 2007.
- [47] * * *, *Natural stone test methods- Determination of compressive strength*, **UNI EN 1926**, Ente Nazionale Italiano di Unificazione (Italian National Unification), 2007.
- [48] * * *, *Standard Test Method for Evaluation of Durability of Rock for Erosion Control Under Wetting and Drying Conditions*, **ASTM D5313**, American Society for Testing and Materials, United States, 2021.
- [49] * * *, *Natural stone test methods—Determination of frost resistance*, **TS EN 12371**, Turkish Standard Institution, Ankara, Turkey, 2010.
- [50] * * *, *Natural stone test methods—Determination of resistance to salt crystallization*, **TS EN 12370**, Turkish Standard Institution, Ankara, Turkey, 2001.
- [51] * * *, *Natural stone test methods—Determination of resistance to ageing by SO₂ action in the presence of humidity*, **TS EN 13919**, Turkish Standard Institution, Ankara, Turkey, 2004.
- [52] F. Becherini, G. Pastorelli, G. Valotto, A. Gambirasi, S. Bianchin, M. Favaro, *Effects of protective treatments on particle deposition and colour variation in stone surfaces exposed to an urban environment*, **Progress in Organic Coating**, **112**, 2017, pp. 75–85, <https://doi.org/10.1016/j.porgcoat.2017.06.029>
- [53] O. Garcia, K. Malaga, *Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on Cultural Heritage porous materials*, **Journal of Cultural Heritage**, **13**, 2012, pp. 77–82, <https://doi.org/10.1016/j.culher.2011.07.004>
- [54] K. Çorapçioğlu, *Taş Ayrışmasının Nedenleri ve Koruma Teknikleri (Causes of Stone Weathering and Conservation Techniques)*, **PhD. Tesis**, Mimar Sinan Üniversitesi, Mimarlık Fakültesi yayını/**Mimar Sinan University, Faculty of Architecture publication**), İstanbul, 1993, 74p.
- [55] J. Hristova, V. Todorov, *Consolidation effect of Wacker silicones on the properties of sandy limestone*, **Proceedings of the 8th International 132 Congress on Deterioration and Conservation of Stone**, Berlin, 1996, pp. 1195-1199.
- [56] G.R. Fife, **Greener Solvents in Conservation: An Introductory Guide by Sustainability in Conservation**, Archetype Publications, UK, 2022.

Received: June 22, 2023

Accepted: July 04, 2024