EFFECT OF ALKOXYSILANE-BASED TREATMENT ON THE DURABILITY OF NORTH CYPRUS STONES FOR CONSTRUCTION

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ABSTRACT

Limestones are generally vulnerable to various weathering effects, hence, protection and consolidation of them is necessary. Locally available limestones of Northern Cyprus have been used in both historical buildings dated back to the 16th century for conservation applications and new buildings mostly as a cladding material. However, certain decay patterns exist on these stones. In the current study, the service life of Cyprus stones was inspected. Alkoxysilane-based consolidation and protection treatments were applied on new quarried stones to enhance the stone properties and aged stones to conserve and protect the architectural heritage. Service life assessment was performed by applying accelerated aging tests on both new and aged stones before and after treatments. The treatments improved the physical, mechanical and durability properties of the stones in terms of unchanging the water vapor diffusion resistance factor, decreasing the porosity and the water absorption ratio, increasing the ultrasound pulse velocity, the compressive and the flexural strengths, and improving the resistance of the stones against wetting-drying, freeze-thaw, salt crystallization and SO_2 vapour effects. The combination of consolidation and protection treatment (K2) was more efficient on the properties of the stones compared to only protection treatment (K1) due to the better penetration capacity, higher decreasing ratio of the porosity, and higher improvement of the physical, mechanical and durability properties. The treatments also improved the properties of the aged stones; thus, it may be inferred that treatment would benefit the conservation of historical buildings.

KEYWORDS

chemical treatment, consolidation, treatment efficiency index (TEI), durability, limestone

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1. INTRODUCTION

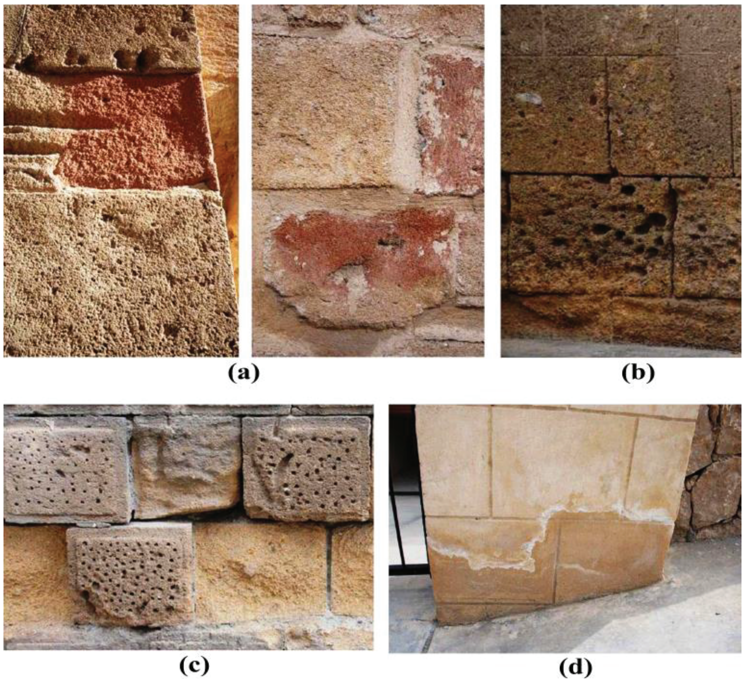
Construction materials and components are required to be durable in order to reduce environmental and economic impact in terms of a sustainable built environment. Therefore, studies on construction material and component durability, service life estimation and assessment methodologies are being carried out in order to extend the service life and maintenance intervals of new buildings and perform efficient renovation for existing buildings. Service life is defined as the period in which a building or its components satisfy performance requirements beginning from its construction [1].

Limestone subjected to exterior exposure of the atmosphere deteriorates due to the weathering effects of wind, rain and thermal change. When water penetrates into the limestone, it may bring about detrimental effects via the dissolution of the carbonate component of the stone. Physical degradation may occur due to freezing-thawing cycles and salt crystallization, and biological degradation [2]. Limestone is highly reactive to acidic rain, with the formation of carbonic and sulphuric acid reactions, which degrade the stone. When limestone has serious decay patterns and cohesion loss, in situ consolidation is necessary, by applying synthetic organic polymers (acrylic polymers and copolymers, epoxies), inorganic stone consolidants (siliceous consolidants such as alkali silicates and fluorosilicon compounds, and alkaline earth hydroxides such as calcium hydroxide and barium hydroxide) and alkoxysilanes, which bind loose grains and fill cracks [3, 4]. The consolidation should improve the mechanical properties, resistance to water dissolution and water erosion, increase the resistance of the stone to deterioration by salt crystallization and freeze-thaw effects, but should not prevent water vapour migration through the stone and not change its thermal expansion coefficient [5].

Alkoxysilane-based compositions have been used for stone consolidation since 1861 [6]. They can penetrate easily into porous material due to their low viscosity. They have lower impact on the permeability and drying properties of the stones than other organic based products [7]. They have strong siloxane bonds that lead to thermal and oxidative stability and withstand ultraviolet solar radiation cleavage. In addition, the light stability of siloxane enables the alkoxysilane-based consolidants to be used outdoors [8]. On the other hand, alkoxysilanes have some disadvantages: They may initially darken the initial colour of the stones [9], or may develop white spots on the stones. Furthermore, their high cost may restrict their use for large projects. Tetraethoxysilane (ethylsilicate or silicic-acid ester), triethoxymethylsilane, and trimethoxymethylsilane are the most used alkoxysilane types for stone consolidation [4]. The reaction between the stone and absorbed alkoxysilane-based compositions consists of two stages which are hydrolysis with water to form silanols and condensation of silanols and formation of siloxane linkages (-Si-O-Si-) which lead to strength increase [4, 7]. The solidified material does not fill the entire pore space; it only coats the pores and thus allows moisture transfer [4].

The limestones of Northern Cyprus are sedimentary rocks quarried from the island and have distinctive texture and colour. The quarries of the stones are still in service and supply stones for the local area. These limestones have been used in both historical buildings dated back to the 16th century for conservation applications and new buildings mostly as a cladding material. However, certain decay patterns exist on Cyprus stones such as staining (general or localized discoloration of the limestone), crumbling (break up or dissolution of the stone which may be caused by inherent weakness of the stone or external factors affecting the strength and durability of the stone), chipping (the separation of small pieces or larger fragments from stone), spalling (separation and breaking away of pieces of stone due to sub-florescence, freeze-thaw, or structural overloading of the stone), peeling (flaking away of the stone surface from

FIGURE 1. Decay patterns of Northern Cyprus limestones: (a) staining (Great Inn, Nicosia); (b) crumbling (Nicosia); (c) chipping (Selimiye Mosque, Nicosia); (d) efflorescence (Kyrenia).



the substrate in layers), efflorescence (the surface deposition of soluble salts as moisture in the stone evaporates) and sub-florescence (internal accumulation of soluble salts deposited under the stone surface as moisture in the wall evaporates) (Figure 1).

The objective of this study is to investigate the service life of Cyprus stones. To achieve this goal, an experimental campaign was performed; protection and consolidation treatments were applied on new-quarried stones to enhance the stones' properties and aged stones to conserve and protect their architectural heritage. The service life determination was performed by applying accelerated aging tests on both new and aged stones before and after treatments.

2. MATERIALS AND METHODS

2.1 Stone Chemical and Mineralogical Characterization

The laboratory experiments were carried out on three different limestones: Karpaz Stone (KS), Meluşa Stone (MS), and Buri Stone (BS). KS has been quarried from the Karpaz region on the northeast, while MS from the Erdemli region on the southeast, and BS from the Alayköy region on the northwest of Cyprus Island (Figure 2a). Figure 2b shows the stone samples from Meluşa, Karpaz, and Buri.

Semi quantitative element analysis of the stone samples was done using Philips PW-2404 model XRF (X-ray Fluoresant spectometer) equipment. The results of these tests are given in Table 1. The CaO content of the stones is approximately 90% indicating that they are limestone. KS and BS are two fossiliferous limestones formed almost exclusively of calcium carbonate with fossil remnants. The colour of BS is sandy due to approximately 3% Fe_2O_3 in its structure. MS presents a micritic-argillaceous matrix with a high content of SiO_2 and Al_2O_3 and clay [10].

FIGURE 2. (a) The regions of the quarried limestones; (b) The samples of the limestones: (KS on the left; MS in the medium; BS on the right).

(a) (b)

2.2 Determination of the Treatment Application Procedure

Two different chemicals commercialized by Wacker were applied to the samples of each stone type [11, 12] (Table 2). Ethyl Silicate-based consolidant is a colorless liquid and used after being diluted with white spirit in the ratio of 1:1. It has low molecular weight, low viscosity and good penetration ability [13]. Silane Siloxane-based protection is a solvent-free silicone concentrate and used after being diluted with white spirit in the ratio of 1:11. In the study, only protection treatment was codded as K1 (K1 = Silane siloxane, SILRES BS280), while consolidant (Ethyl Silicates, SILRES BS OH100) + protection (Silane siloxane, SILRES BS280) treatment was codded as K2 (K2 = SILRES BS OH100 + SILRES BS280).

Different treatment methods were applied namely, by brushing (1 and 2 layers), by spraying, and by full immersion (1 s. and 15 min.) in order to determine the most suitable application procedures (Figure 3). All of the application methods were applied as per the instructions given by the producer. The main prerequisite for the successful application is to achieve enough penetration depth. This was provided by the application of treatment until the building material is fully saturated, i.e., it is unable to absorb any more of the treatment. Hence, in the brushing method, application in 2 layers was needed. The spraying method was applied by spray bottle at a distance of 10 cm. In the full immersion treatment of K1, the samples were positioned horizontally in a plastic container and left to absorb it for 15 minutes. After immersion, samples were kept in the lab conditions (20°C, 50% RH) for polymerization period of four weeks. In

TABLE 1. Chemical compositions of KS, MS, and BS.

Component	CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3	CuO	Na_2O	K_2O	TiO_2	P_2O_6	SrO	Cl	Cr_2O_3	SO_3	ZnO
KS (%)	94.45	0.99	0.63	1.75	0.42	0.85	0.02	0.01	0.01	0.21	0.16	0.10	0.14	0.18	0.03
MS (%)	87.40	5.86	1.44	0.90	2.07	0.86	0.02	0.23	0.10	0.32	0.24	0.09	0.17	0.19	0.04
BS (%)	91.67	2.18	2.82	1.03	0.58	0.85	0.02	0.01	0.02	0.30	0.12	0.09	0.14	0.14	0.03

TABLE 2. Properties of the chemicals [11, 12].

Product	Property	Inspection method	Value
Ethyl Silicates (SILRES® BS OH 100) [12]	Density at 25°C	DIN 51757	approx. 0.977 g/cm³
	Flash point	ISO 2719	40°C
	Ignition temperature (liquids)	DIN 51794	230°C
	Ethyl Silicate content		approx. 100 wt.%
Silane-Siloxanes (SILRES® BS 280) [11]	Density at 25°C	DIN 12791	1.041–1.06 g/cm³
	Flash point		49°C
	Ignition temperature (liquids)	DIN 51794	260°C
	Viscosity, dynamic at 25°C	DIN 51562	7–9 mPa.s
	Silane/Siloxane content		approx. 100 wt.%

K2 treatment, the samples were horizontally placed in the consolidant for 15 minutes and kept in the lab conditions (20°C, 50% RH) for two weeks. Afterwards, they were left to absorb K1 for 15 minutes and again kept in the lab conditions for another two weeks. The amount of penetrated treatment is measured by the mass gain of the stones divided by per unit surface [kg/m^2].

The type and the characteristics of the stone and chemicals, environmental conditions, and consolidation processes are important parameters for the performance of consolidation [7]. The amount of the treatment loading is also an important parameter. Excessive loading will reduce the stone porosity and water vapor transmission. The minimum loading required to achieve performance goals should be determined experimentally. Simple gravimetric determination of the mass increase of a stone following immersion in water is a widely accepted method to determine the change in water absorption of stone after consolidation, as a function of time. Treatment of stone with a hydrophobic consolidant will reduce the water absorption appreciably. Estimation of the improvement in the mechanical properties of stone following treatment may be obtained from the measurement of compressive strength which can be related to specific performance requirement for treated stones [5]. Thus, in this study, the effectiveness of applied methods was evaluated in terms of decreasing the water absorption ratio, increasing the compressive strength, and the amount of penetrated treatment by the samples. The most suitable application method that justified the treatment selection criteria for the three types of stones was determined as "immersion for 15 minutes" according to the test results highlighted in Table 3.

FIGURE 3. Applied treatment methods: (a) brushing; (b) spraying; (c) immersion.

(a) (b) (c)

TABLE 3. The influence of the application procedures on the properties of stones.

Treatment	Water absorption by weight (%)						Compressive strength (MPa)						Amount of penetrated treatment (kg/m^2)					
	KS		MS		BS		KS		MS		BS		KS		MS		BS	
Methods	K1	K2	K1	K2	K1	K2	K1	K2	K1	K2	K1	K2	K1	K2	K1	K2	K1	K2
Ref	9.1	9.1	15.9	15.9	17.5	17.5	15.0	15.0	19.0	19.0	4.8	4.8	—	—	—	—	—	—
Brushing (1 layer)	1.8	**0.6**	2.2	2.2	13.3	1.6	15.9	**21.9**	**20.9**	14.5	5.1	4.6	0.16	0.22	0.11	0.18	0.24	0.28
Brushing (2 layer)	0.6	0.8	2.1	2.3	0.9	1.4	14.7	15.5	15.4	21.5	4.8	4.0	0.24	0.29	0.21	0.28	0.31	0.39
Spraying	5.3	3.5	3.5	3.5	13.9	4.5	16.3	15.2	15.4	16.1	4.6	4.5	0.04	0.09	0.02	0.06	0.11	0.18
Immersion (1 s.)	0.6	0.7	2.2	**1.9**	1.0	1.3	18.1	17.1	19.1	17.3	5.6	5.3	0.52	0.86	0.31	0.63	0.62	1.07
Immersion (15 min.)	**0.6**	0.9	**1.9**	2.1	**0.8**	**1.1**	**18.1**	18.0	19.4	**22.0**	**6.7**	**6.0**	**0.89**	**1.16**	**0.48**	**0.92**	**0.99**	**1.55**

2.3 Physical, Mechanical and Durability Tests

Experimental study consists of three stages: (i) Determination of physical and mechanical characteristics of quarried stones; (ii) Determination of durability properties of stones; (iii) Determination of efficiency of the treatments on the durability properties of the new and aged stones (Figure 4). The durability tests on the aged stones were carried out in order to determine whether the treatment would be a benefit to the conservation of historical buildings. Each test result is the average of six samples.

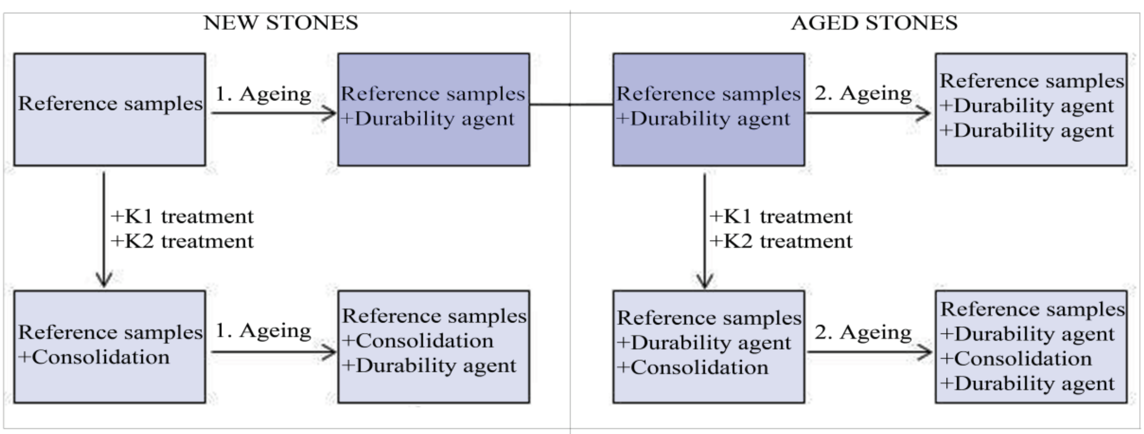
The capillarity coefficient test was applied according to the Turkish Standard TS EN 1925:2000 [14]. The samples were dried to a constant mass at 70°C and placed in 3 mm water on their base. The timer device started and at time intervals the samples were removed from the water and weighed. The capillarity coefficient was calculated by using the formula: $C = (mi - md)/A.(t)^{1/2}$ where md is the mass of the dry sample, mi successive masses of the sample during testing, A area of the side immersed in water, and t times.

The water absorption ratio of the stones was determined by applying Turkish Standard TS EN 13755:2009 [15]. The samples were dried to a constant mass at 70°C, weighed and placed in a container. Tap water at 20°C was added up to half the height of the samples. After 60 min, tap water was added until the level of the water reached three-quarters of the height of the samples. After 120 min, the samples were completely immersed in water for 48h. The water absorption ratio was calculated by using the formula: $Ab = [(ms - md)/md] \times 100$ where ms denotes the mass of the saturated sample and md is the mass of the dry sample.

Determination of water vapor transmission properties of the stones was carried out by applying the test method of the Turkish Standard TS EN 12086:2002 [16]. The samples were sealed to the open side of a test dish containing a desiccant and were placed in a test atmosphere whose temperature and humidity were controlled. Periodic weighing of the samples was conducted. After the test, change in mass, water vapour transmission rate, water vapour resistance, water vapour permeability, and finally the water vapour diffusion resistance factor of the stones were calculated step-by-step.

An ultrasound pulse velocity (UPV) test was applied according to the Turkish Standard TS EN 14579:2006 [17]. The samples were dried at 70°C. A good acoustical contact was ensured by the use of grease to the stone surface. An electronic device named Proceq was used and repeated

FIGURE 4. Experimental process applied to the stones.



readings of the transit time were made until a minimum value was obtained. Transmissions of the pulse velocity was calculated from the formula: $V = L/t$ where V pulse velocity in km/s, L path length in mm, and t time taken by the pulse to transverse the length in μs.

The flexural strength of the stones was determined by applying Turkish Standard TS EN-12372: 2001 [18]. The samples were dried at 70°C and placed centrally on the two rollers and the loading roller was placed in the middle of the samples. The load was increased uniformly at a rate of 0.25 MPa/s until the samples broke. The flexural strength was calculated using the equation: $R = (1.5 \times F \times l)/(b \times h^2)$ where F is break in load, l is distance between the rollers, and b and h denote the width and thickness of the sample, respectively.

A compressive strength test was applied according to the Turkish Standard TS EN-1926:2000 [19]. The samples were dried at 70°C and the load on the samples was applied continuously at a constant stress rate of 1 MPa/s until the maximum load was reached. The compressive strength was calculated by: $R = F/A$ equation where F denotes the failure load, in Newtons; A is the cross-sectional area of the sample before testing in mm^2.

Wetting and drying enables evaluation of the behavior of stones when subjected to weathering stemming from repetitive wet and dry cycles. The samples were subjected to 20 wet-cycles according to Turkish Standard TS EN 14066 [20]. Each cycle consisted of drying the samples at 70°C for 18 h and then submerging them in tap water at 20°C for 6 h.

The salt crystallization test enables determination of the resistance to salt attack of the stones. The samples were immersed in a 14% w/w Na_2SO_4 solution at 20°C for 2 h according to the Turkish Standard TS EN 12370 [21]. They were then removed from the solution and were dried at 105°C for 20 h. Afterwards, they were left to cool to room temperature for 2 h. The samples were subjected to 15 cycles.

Freeze-thaw cycling allows determination of the resistance to pressures in the stones derived from increasing of specific volume when the water passes from liquid to ice. The samples were exposed to 20 freeze-thaw cycles according to the Turkish Standard TS EN 12371 [22]. Each cycle composed of freezing under atmospheric conditions at −12°C for 6 h, followed by thawing in water at 20°C for 6 h.

Ageing by the sulphur dioxide (SO_2) action test is a method to assess the resistance of stones to damage by extreme environmental conditions in the presence of pollutant gases according to the Turkish Standard TS EN 13919 [23]. The samples were placed in a closed container with 5% sulphur dioxide concentration for 21 days.

The efficacy of the treatment was expressed by the treatment efficiency index (TEI) as a percentage as seen below:

$TEI = (Xp_i / Xp_a) \times 100$ where Xp_i denotes initial value of the property and Xp_a is the value after treatment.

3. RESULTS AND DISCUSSION

3.1 Properties of the Stone: Karpaz, Meluşa, Buri

The properties of the stones are given in Table 4. They are under the category of low-density limestone in accordance with Specification ASTM C568 [24]. Like all sedimentary rocks, limestones contain impurities that affect their appearance and properties. MS has a fine-grained texture and lack of visible particles, while KS and BS have a coarser texture. On the other hand, BS has lower mechanical strengths than KS, which may be the result of its higher porosity, water absorption ratio and capillary coefficient. It may be stated that the pores of BS are open to water ingress and contribute to water permeability [25]. The highest porosity, although representing a stone weakness material, provides some favorable features such as workability, lightness, and obtaining good thermal and acoustic insulation [13]. MS has the highest mechanical strength. Its lowest capillary coefficient may indicate that it has relatively coarse pore structure that increases its water absorption.

Water vapor diffusion resistance factors (μ) of KS, MS and BS were found to be 9, 11, and 23 respectively. These values of (μ) shall be accepted as low when compared with the 20–200, given for the limestone having the density range of 1700–2200 g/cm^3 [26]. The highest vapor resistance of BS may be the result of its highest cylindrical capillary pore structure in which the vapor may be adsorbed by the internal surfaces of the pores and not be permitted to flow through the entire thickness of the material [27].

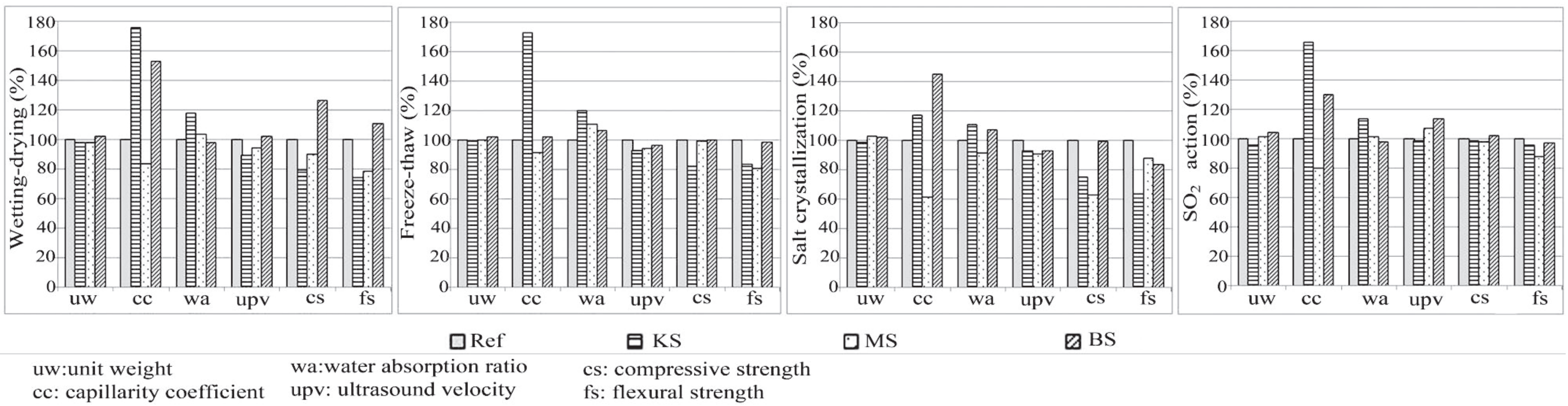
The saturation coefficient is a ratio between apparent porosity and real porosity of a material and indicates how much of its pores filled with water. Frost action occurs when water enters tiny cracks in the stone and freezes at lower temperatures. Ice expands about 10% when it freezes. When water entirely fills the pores then there won't be enough space for expansion and ice exerts a pressure that weaken the stone fabric after a period of time. Hence, the frost resistance of a material depends on 80% or lower values of saturation coefficient [28]. The stones of this study have lower saturation coefficients than 80% and are therefore meant to be frost resistant, but still mechanical properties are important.

KS and MS have a higher strength than 5 MPa and can be used as a load-bearing material [29]. As a cladding material, the stone slabs must have sufficient thickness to resist bending under local horizontal wind loads. Thickness depends partly on the size of the slabs and the spacing of the fixing cramps and partly on the flexural strength of the stone. If we assume the stones of this study are cut as a cladding panel having the same size and panel span between

TABLE 4. Properties of the stones and general requirements to the selection of limestone for general building and structural purposes.

		Unit weight (uw) (g/cm^3)	Specific weight (g/cm^3)	Porosity (%)	Capillarity coeff. (10^3) (cc) (cm^2/s)	Water absorption (wa) (%)	Water vapor dif. Resistance factor (μ)	Saturation coefficient (%)	Ultrasound pulse velocity (UPV) (km/s)	Compressive strength (cs) MPa	Flexural strength (fs) (MPa)
Karpaz Stone		1.86	2.72	31	1.12	9.09	9	54	2.98	15.09	6.09
Meluşa Stone		1.47	2.41	39	0.36	15.9	11	60	2.77	19.00	6.13
Buri Stone		1.55	2.64	42	3.16	17.5	23	65	2.49	4.83	2.50
ASTM C568 [24]	Low Density Class	1.76	—	—	—	12	—	—	—	12	2.9
	Medium Density Class	2.16	—	—	—	7.5	—	—	—	28	3.4
	High Density Class	2.56	—	—	—	3	—	—	—	55	6.9

FIGURE 5. Relative properties of the new stones after durability tests.



fixings, higher flexural strengths of KS and MS enable them to be cut in the thickness of 20 mm; on the other hand, BS with its lowest flexural strength should have the thickness minimum of 30 mm [30].

3.2 Durability of the Stone: Karpaz, Meluşa, Buri

Relative properties of the stones after durability tests are given in Figure 5. The apparent rise in the capillarity coefficient of KS and BS after each aging test may be the clue to the new, narrow and interconnected pore development in their fossiliferous structure. Particularly after the wetting-drying test there is an apparent increase in the mechanical properties of BS, which may indicate the soluble compounds clogged in the pores happened by the cycles of wetting-drying. This may be proven by the execution of further microscopic tests. On the other hand, the already low capillary coefficient of the micritic clay structure of MS is decreased further due to the increase of its pore size after aging tests. Indeed, after the 11th cycle of salt crystallization test, MS fragmented (Figure 6). This may be the result of internal pressure that occurred by the crystallization of salts in the drying phase, which are absorbed within the pores. Although KS and BS preserved their integrity, some cracks at the edges of the samples were observed. After the freeze-thaw test, KS and MS could not resist the internal pressure of the ice due to their lower porosity. On the other hand, no significant change is observed in the mechanical properties of BS; this may be attributed to the inherent pore structure of BS that provides enough space to absorb the internal stress of ice expansion. After 21 days of exposure to the water vapor with 5% SO_2 concentration, a slight discoloration of the stones was observed.

Consequently, although the three types of stones analyzed in this study have adequate properties to use in modern architectural applications, since there is some degradation observed in their physical and mechanical properties after durability tests, application of protective treatment prior to use in construction would be suitable to enhance their service life.

FIGURE 6. Meluşa Stone after the 11th cycle of salt crystallization test.

3.3 Influence of the Treatment on the Properties of the Stone: Karpaz, Meluşa, Buri

K1 and K2 treatment reduced the water absorption ratios by 87–92%, and the capillarity coefficients by 97–99% for all the three types of stones (Figure 7). These results are also consistent with the study, which determined that silane siloxane-based protection decreased the water absorption ratio of the stone by 80–90% [31]. After K1 and K2 treatment, the (μ) factors of the KS, MS and BS stones decreased approximately 6% and 5% and can be accepted as negligible. Indeed, the combination of consolidant and protection treatment, like K2, should decrease the (μ) factor of the original stone 10–25% at most [32].

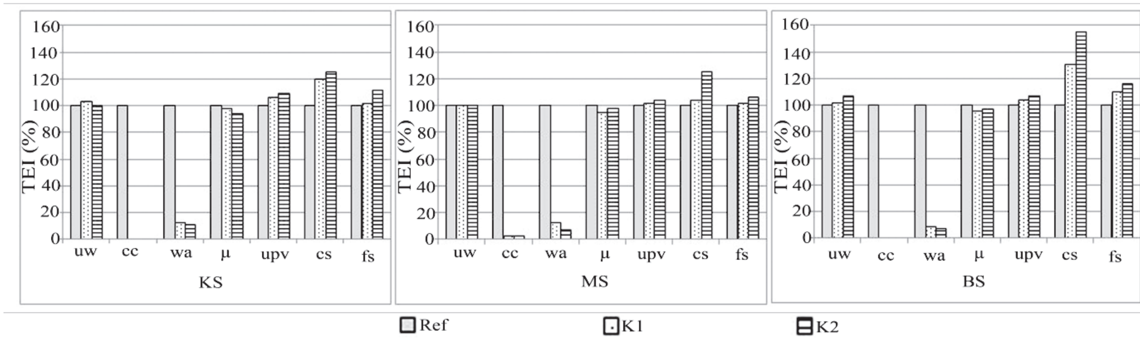
TEI of the K1 and K2 treatments regarding the UPV are 6% and 10% for KS, 1% and 3% for MS, and 4% and 5% for BS, respectively; the influence of K2 treatment is higher than K1 treatment. Accordingly, TEI of the K1 and K2 was found to be 15% and 30% respectively on the UPV of the stones, depending on their porosity [33]. The mechanical properties of all stones increased contrary to their porosity, water absorption, and capillarity coefficient values. Although BS has the most porous structure (42%), the highest mechanical improvement (35%) was observed after K2 treatment which may be due to the increase in penetration depth of K2. The increase of its UPV is also an indicator of its relatively compact internal structure obtained after K2 treatment. In line with these results, it can be inferred that both treatments are found to be favorable and to increase the mechanical properties of all three type of limestones.

3.4 Influence of the Treatment on the Durability Properties of the Stone

3.4.1 New stone: Karpaz, Meluşa, Buri

When the influence of treatment on the wetting-drying resistance of new stones is analyzed, it is observed that the physical and mechanical properties of the treated KS and MS was enhanced, while those of the BS remained almost same (Figure 8). The properties of the untreated BS increased after the wetting-drying test; hence, a decrease of the treatment efficiency on BS is an expected result. After the wetting-drying test, as indicators of a compact structure of a material, UPV and unit weights remained almost the same in both treated and untreated stones. There is approximately a 10% increment in UPV parallel to the increase in mechanical strengths of the KS and MS. In terms of durability improvement, K2 treatment is more efficient than K1.

FIGURE 7. The influence of the K1 and K2 treatment on the properties of the stones.



uw: unit weight
cc:capillarity coefficient
wa: water absorption
upv: ultrasound velocity
cs: compressive strength
fs: flexural strength
μ: water vapour diffusion resistance factor

The properties of the new stones were enhanced after both treatments under the freeze-thaw effect. K1 and K2 treatment reduced the water absorption ratio by 78% and 84%, respectively. There is also an increase in the compressive strengths, which indicates the efficiency of the treatments. TEI of K2 treatment is 50% higher than that of K1. The affirmative influence of both treatments on the properties, were seen mostly on KS, then followed by BS and MS respectively.

Salt crystallization was the most destructive test on untreated stones. In Figure 9, after the salt crystallization test, treated and untreated new stones can be seen. However, both treatments enhanced the properties of the stones along with keeping their integrity; K1 and K2 treatments decreased the water absorption ratio 78%, and 81%, respectively. Untreated MS, which was totally disintegrated after 11 cycles (Figure 6), exhibited the highest performance under the salt crystallization test after being treated with K1 and K2.

Under the effect of SO_2 vapor, UPV and unit weight values of all new stones treated by K1 and K2 remained almost same; water absorption ratios decreased by 14% with K1, and 18% with K2, and gives better results compared to K1. The TEI index decreased gradually from BS, KS to MS, respectively.

Consequently, the chemical treatments generally enhance the durability properties of the Cyprus limestones. Similar results were reported in the literature. For example, a research team examined ten sites where chemical treatments were applied primarily with Brethane (a type of alkoxysilane consolidating material produced at the UK Building Research Establishment) [34] after approximately twenty years. The results of the survey revealed that the properties of the treated limestones were better than untreated stones, regardless of the type of limestones (siliceous, sandy, calcareous or dolomitic limestones) [8]. Thus, it may be inferred that the properties of Cyprus limestones will be maintained for many years after chemical treatments.

3.4.2 Aged stone: Karpaz, Meluşa, Buri

The influence of the K1 and K2 treatments on the durability of aged stones is given in Figure 10 after being obtained from the wetting-drying and freeze-thaw tests.

After the wetting-drying test of aged KS, MS and BS, both K1 and K2 treatments lead to a significant decrease in capillarity coefficient (90–100%) and water absorption (80%). This may indicate that chemical treatment filled the open and capillary pores. The development seen in physical properties of the stones are in conformity with the compressive strength results, which give important clues about a material's stability. This shows that the treatments have positive effects on the old stones.

After the freeze-thaw test, water absorption ratios of all stones decreased 85–90% depending on the decrease in capillary pores. The compressive strengths of all stone types increased after treatments. The decrease in the flexural strengths of KS and MS after K1 treatment indicates the brittleness of the stones. TEI of K2 is higher than K1 and BS performed better followed by MS and KS, respectively.

Figure 11 reveals the compressive strengths of new and aged stones before and after the application of chemical treatments K1 and K2. Under both aging agents, treatment efficiency indexes of K1 and K2 for all three types of stones was improved and helped to enhance the strengths, although higher values were obtained with the K2 treatment. The interesting point is that after both aging tests, TEI of the treatments on strengths is gradually decreasing from KS, MS to BS in "new" stones, while there is a gradual increase from KS, MS to BS in "aged" stones. Besides, for all stone types, TEI of the chemical treatments was found to be highest for

FIGURE 8. Influence of the treatment (K1 and K2) on the properties of the new stone: Karpaz, Meluşa and Buri Stones.

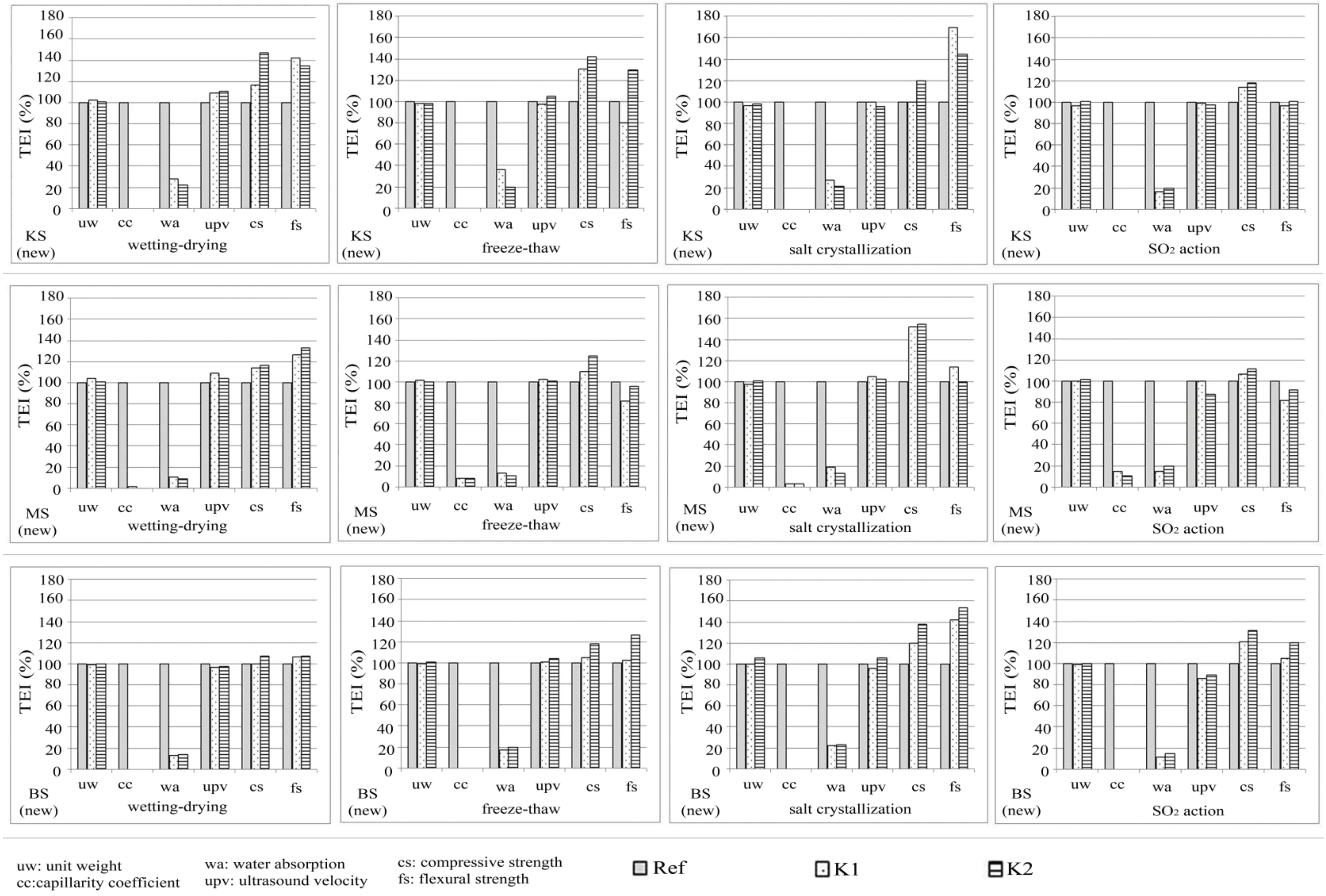


FIGURE 9. Treated and untreated new stones after salt crystallization test: (KS on the left; MS in the medium; BS on the right).

FIGURE 10. Influence of the treatment (K1 and K2) on the properties of aged stone: Karpaz, Meluşa and Buri Stones.

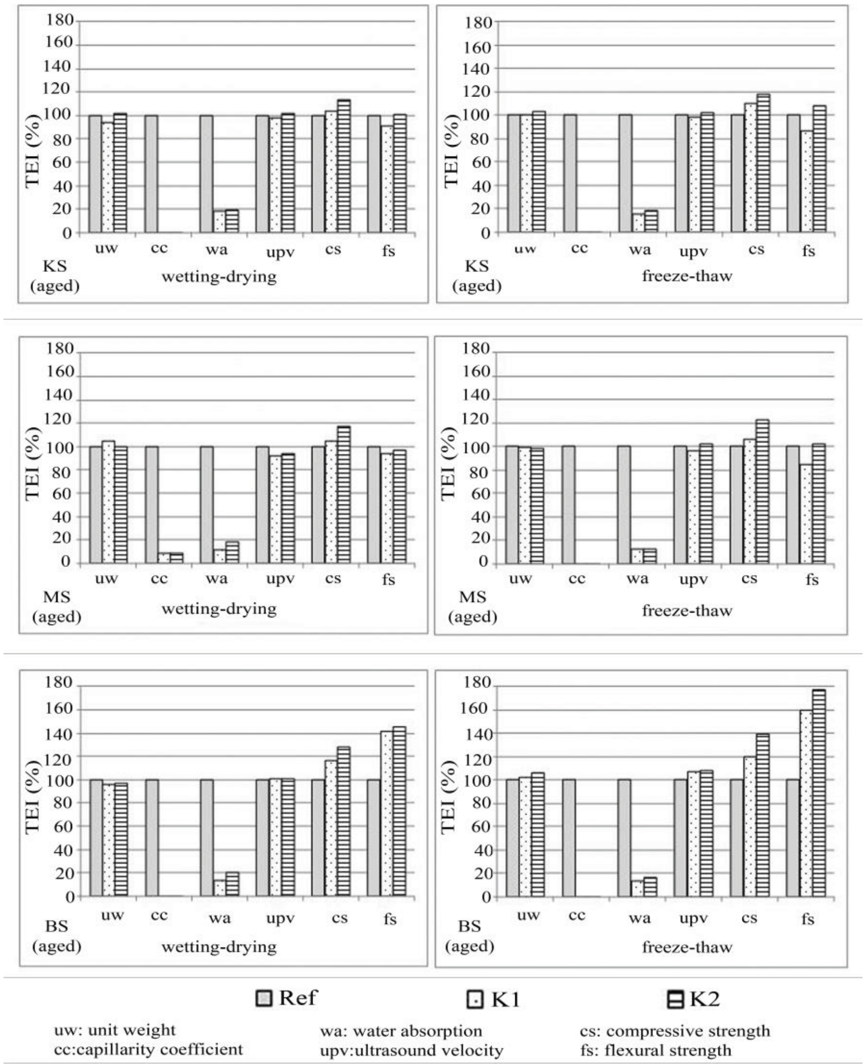
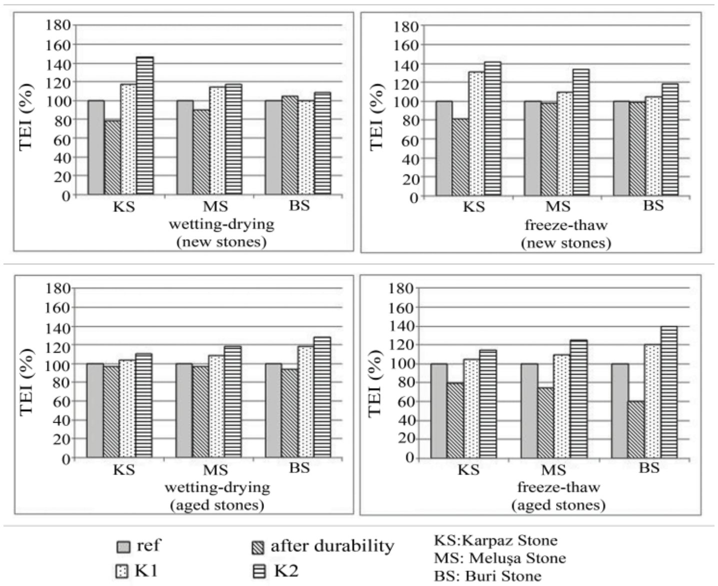


FIGURE 11. TEI of the treatments on the compressive strengths of new and aged stones.



the stones having the lowest compressive strength following the aging tests. Hence, the higher the degradation degree under durability tests, the higher the TEI of the treatments (Table 5). Therefore, it can be stated that prior to use of new-quarried limestones in architecture, chemical treatment application is efficient in enhancing the service life of the stones.

4. CONCLUSION

The following conclusive remarks can be stated from the obtained results:

- All three types of stones tested can be categorized as low density limestone. The mechanical characteristics of the micritic-argillaceous Meluşa Stone are higher than those of the fossiliferous Karpaz Stone and Buri Stone. However, Buri Stone represents lower

TABLE 5. Influence of the treatment on the durability properties of the stones: new and aged.

Durability tests		Wetting-Drying			Freeze-Thaw			Salt Crystallization			SO_2 action		
Treatment Type		Ref	K1	K2	Ref	K1	K2	Ref	K1	K2	Ref	K1	K2
New stones	Good	BS	KS	KS	BS	KS	KS	BS	MS	MS	MS	BS	BS
	↓	MS	MS	MS	MS	MS	MS	KS	BS	BS	KS	MS	MS
	Bad	KS	BS	BS	KS	BS	BS	MS (decayed)	KS	KS	BS	KS	KS
Aged stones	Good	KS	BS	BS	KS	BS	BS	—	—	—	—	—	—
	↓	MS	MS	MS	MS	MS	MS	—	—	—	—	—	—
	Bad	BS	KS	KS	BS	KS	KS	—	—	—	—	—	—

mechanical properties due to its higher capillarity and porosity. All three types of Cyprus Stones have adequate properties for use in modern architectural applications, while Karpaz Stone and Meluşa Stone fulfill the requirements of a load-bearing wall material.

- The stones respond in a different manner to accelerated durability tests. Karpaz Stone and Meluşa Stone with a lower capillarity coefficient and porosity show degradation due to the internal pressures formed during durability tests. Karpaz Stone is the most degraded stone after wetting-drying and freeze-thaw tests, while Meluşa Stone is the most degraded stone after salt crystallization. On the other hand, Buri Stone, having the highest capillarity coefficient and porosity, is affected slightly after durability tests due to its pore structure.
- Silane Siloxane-based protection treatment (K1) and the combination of Ethyl Silicate-based consolidant and Silane Siloxane-based protection treatment (K2) improve the physical, mechanical and durability properties of all three types of the stones in terms of: unchanging the water vapor diffusion resistance factor, decreasing the porosity and the water absorption ratio, increasing the UPV, the compressive and the flexural strengths, and improving the resistance of the stones against wetting-drying, freeze-thaw, salt crystallization and SO_2 vapor effects. Thus, treatment application prior to the use of the stones would be a better solution to enhance their service life.
- Generally, (K2) type treatment decreased the water absorption ratios and increased the mechanical strengths of the three types of stones than (K1). These results obtained are valid for new stones treated by (K2), and stones aged by durability tests.
- Treatments also improve the physical, mechanical and durability properties of the aged stones. Thus, it may be inferred that treatment would yield a benefit to the conservation of historical buildings. Staining, crumbling, chipping, and efflorescence deterioration types seen in the Cyprus stones can be prevented with treatment.
- The higher the degradation degree under durability tests, the higher the TEI of the treatments of the stone which are either new or aged stones.
- Due to the fact that the TEI of the treatments on the compressive strength of the new stones are higher than those of the aged stones, it may be concluded that using new-quarried limestones after treatment would be more sustainable.

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