

GÖKHAN EKİNCİOĞLU<sup>1</sup>

## Non-destructive methods determination of thermal shock resistance of natural building stones applied with different water repellent chemicals on their surfaces

### Introduction

Due to their durability and aesthetic appearance, natural stones are used in many applications and are exposed to various atmospheric conditions such as rain, wind, humidity, freeze-thaw cycles, and temperature differences between day and night, depending on their areas of use. Atmospheric factors cause unfavorable changes in both the physico-mechanical properties and the external appearance of natural stones. These types of deterioration in the structure of natural stones make repairs necessary, and these processes also increase construction cost (Erdoğan and Yaşar 2001; Akbay et al. 2012).

In cases where protective measures are not taken against the effects of changing atmospheric conditions, over time, pollution, blooming, erosion, and dissolution occur on the

✉ Corresponding Author: Gökhan Ekinciog; e-mail: gokhanekincioglu@gmail.com

<sup>1</sup> Kırşehir Ahi Evran University, Kaman Vocational School, Department of Mining and Mineral Extraction, Turkey; ORCID iD: 0000-0001-9377-6817; e-mail: gokhanekincioglu@gmail.com



© 2023. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike International License (CC BY-SA 4.0, <http://creativecommons.org/licenses/by-sa/4.0/>), which permits use, distribution, and reproduction in any medium, provided that the Article is properly cited.

surface of natural stones due to the effects of acid and sulfate in the air and water. As a natural consequence, color and pattern distortion is observed in the structure of coating materials (Figure 1) (Çetin 1998; Butler and Likens 2019; Yeşilay 2019). Chemical reactions resulting in wear and color changes are more frequently observed, especially in carbonate rocks. Figure 1 shows the appearance of a building where limra limestone and travertine are used as exterior cladding, and color changes are also observed in the limra limestone slabs.



Fig. 1. View of a building where limra limestone and travertine are used as exterior cladding (Kırşehir Ahi Evran University)

Rys. 1. Widok budynku, w którym jako okładzinę zewnętrzną zastosowano wapień limra i trawertyn (Uniwersytet Kırşehir Ahi Evran)

One of the most important factors in color changes and deterioration in natural stones is the water it absorbs. Water that penetrates into natural building stones in different ways can cause weathering in the rock as a result of wetting-drying, freezing-thawing, and salt crystallization. When water enters a stone's pore system, various salt solutions carried in the water can cause salt crystallization, usually due to evaporation (Coussy 2006).

Cycles that occur during day and night temperature differences or due to climate differences can cause salt crystals to grow. In this case, large numbers of salt crystals can form in solutions with high salt concentration (Thaulow and Sahu 2004). Micro-cracks can form due to high pressures caused by salt crystallization in closed pores. The risk of salt damage in building materials depends on the degree of pore filling by crystals and the magnitude of the crystallization pressure (Derluyn et al. 2014; Çelik et al. 2019).

In recent years, different water-repellent chemicals have been used to protect natural stones against deteriorations caused by atmospheric conditions. Water repellents are chemi-

cal products that reduce the water absorbency of the surface, in order to minimize the effects of formations that could damage the structure of the stone, such as water and salts carried by water, when exposed to atmospheric conditions. In other words, they are products that make the surface of natural stone hydrophobic.

There are studies in the literature that have investigated the water absorption of natural building stones using protective chemicals in laboratory conditions (Charola 1995; Bromblet and Martinet 2002; Vallet et al. 2000; Ioannou and Hoff 2008; Kılıç and Gültekin 2009; Thomachot Schneider et al. 2011; Pinna et al. 2011; Licchelli et al. 2013; Ersen et al. 2013; Pérez et al. 2014; Tulliani et al. 2014; Çelik et al. 2018, 2019).

Within this study, different water-repellent chemicals were applied to samples of limra limestone and travertine, which are preferred as exterior cladding in architecture. The aim has been to increase the service life of the natural stones with surfaces that were made hydrophobic by delaying their deformations.

## 1. Materials and methods

In this study, two different rocks of carbonate origin (limra limestone and travertine) from Turkey were used. Limra limestone samples were obtained from the Antalya region and travertine samples were obtained from the Denizli region (Table 1).

Table 1. Origin of carbonate rocks used in the study

Tabela 1. Pochodzenie skał węglanowych wykorzystanych w badaniach

Sample name	Region	Geological origin
Limra limestone	Antalya	Sedimentary
Travertine	Denizli	Sedimentary

The obtained natural stones were brought to the natural stone analysis laboratory of the Kaman Vocational School of Ahi Evran University's in Kırşehir, where samples measuring  $2 \times 10 \times 10$  cm were prepared. A total of thirty samples were prepared and five samples from each group were used. After sample preparation, two different water-repellent chemicals were provided from the TEKNO Building Chemicals company: one water based and the other solvent based. The water-based repellent chemical has a thick consistency and is white in color (Figure 2a), while the solvent-based chemical is more fluid and has a transparent appearance (Figure 2b).

Before the application of water repellent chemicals, the surfaces of the obtained samples were cleaned using a soft brush in pure water. The surface cleaning process was conducted



Fig. 2. Appearance of water-repellent chemicals  
a) water-based water repellent, b) solvent-based water repellent

Rys. 2. Wygląd środków hydrofobowych  
a) środek hydrofobowy na bazie wody, b) środek hydrofobowy na bazie rozpuszczalnika

to enhance the impregnation performance of the water-repellent chemicals. Water-repellent chemicals were applied to all surfaces of the samples with a brush, in two coats with a 4-hour interval, in dimensions of  $2 \times 10 \times 10$  cm (Figure 3). The application was conducted at  $20^{\circ}\text{C}$  and 40% humidity, in accordance with the application conditions of the TEKNO company (TEKNO Construction Chemicals Catalog 2022).

Both chemicals resulted in a shiny appearance on the surfaces of the samples after their application. However, as the water repellency absorption was completed, the surfaces returned to their previous appearance. No significant color change was observed upon examination with the naked eye. After the application, samples were left for a period of approximately one week in order to dry.



Fig. 3. Water-repellent chemical application process  
a) water-based water-repellent chemical application, b) solvent-based water-repellent chemical application

Rys. 3. Proces aplikacji środka chemicznego hydrofobowego  
a) aplikacja środka chemicznego hydrofobowego na bazie wody,  
b) aplikacja środka chemicznego hydrofobowego na bazie rozpuszczalnika

Pure water absorption tests were conducted on the samples before the thermal shock experiments with salt solution to determine their hydrophobicity. Figure 4a presents an example of a sample without the application of a water-repellent chemical; Figure 4b presents an example with the application of a water-repellent chemical. The sample without the application of a water-repellent chemical releases air as a result of water entering its pores. This was observed with air bubbles formed on the surface of the stone. However, no air bubbles were observed on the sample with the application of a water repellent chemical.

Descriptions of the samples used in the experiments are presented in Table 2.

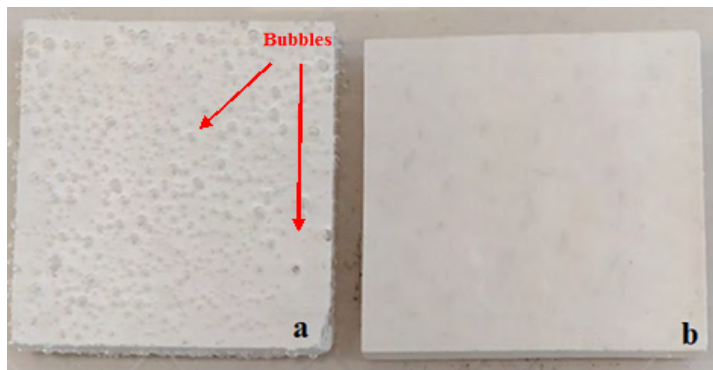


Fig. 4. The appearances of examples with and without water repellent applied in water a) without water-repellent chemical, b) with water-repellent chemical

Rys. 4. Wygląd przykładów z i bez środka hydrofobowego zastosowanego w wodzie a) bez środka chemicznego hydrofobowego, b) ze środkiem hydrofobowym

Table 2. Codes of the samples used in the experiments

Tabela 2. Kody próbek użytych w doświadczeniach

Sample code	L-O	L-SO	L-SB	TRV-O	TRV-SO	TRV-SB
Sample description	Limra limestone water-repellent chemical is not applied (Control samples)	Limra limestone solvent-based water-repellent chemical applied	Limra limestone water-based water-repellent chemical applied	Travertine water-repellent chemical is not applied (Control samples)	Travertine solvent-based water-repellent chemical applied	Travertine water-based water-repellent chemical applied

After the preparation of the samples, the determination of the resistance to thermal shock was performed in accordance with the principles stated in TS EN 14066. The cycles were repeated twenty times, and a 14% NaCl solution was used instead of pure water.

Before the cycles began, the mineralogical and geochemical analyses of the samples, as well as their weights (for samples dried to constant mass), ultrasonic velocities, Leeb hardness values, and color values were measured. The color values of the samples were measured again every five cycles to monitor changes in these values. Weight changes, ultrasonic velocities, and Leeb hardness values were also measured after the thermal shock test and compared with the pre-test data. In addition, SEM and EDX analyses were conducted before and after the thermal shock tests.

## 2. Results of experimental studies

### 2.1. Mineralogical and chemical analysis

Thin-section analyses were conducted to determine the mineralogical and petrographic properties of the obtained samples. During the examinations, a transmitted-light polarizing microscope with bottom illumination manufactured by ZEISS was used in the thin-section

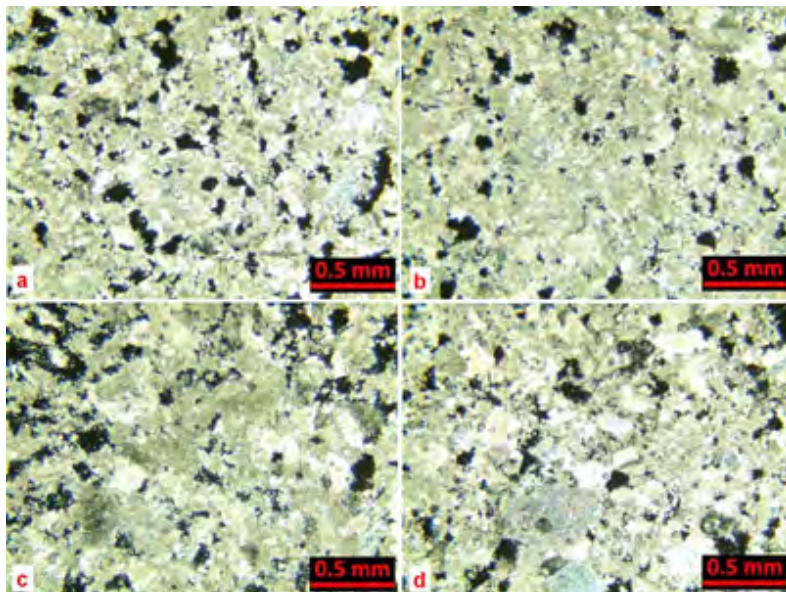


Fig. 5. Thin-section double-nicol images of limra limestone samples  
a) original sample, b) sample without water-repellent chemical after thermal shock,  
c) sample with solvent-based water-repellent applied, d) sample with water-based water-repellent applied

Rys. 5. Cienkowarstwowe obrazy podwójnego nikolu próbek wapienia limra  
a) próbka oryginalna, b) próbka bez środka hydrofobowego po szoku termicznym,  
c) próbka z nałożonym środkiem hydrofobowym na bazie rozpuszczalnika,  
d) próbka z nałożonym środkiem hydrofobowym na bazie wody

laboratory of the Department of Geological Engineering at Ahi Evran University in Kırşehir. The cross-polarized images of the limra limestone samples obtained from the thin-section examinations are shown in Figure 5, and those of the travertine samples are shown in Figure 6.

Analyzed in thin sections, both rocks were observed to have fine-grained calcite minerals (sparite) and abundant pores, indicating that they were limra limestones (Figure 5a and Figure 6a). In addition to the original rock samples, thin-section analysis was also conducted on the samples subjected to thermal shock tests with and without the application of water repellents in order to determine their effects (Figure 5b, c, d and Figure 6b, c, d). However, no data reflecting the protective properties of water-repellent chemicals could be obtained from the thin-section analysis.

In addition to the thin-section analyses of the samples, geochemical analyses were performed with the XRF device at the ASÜBTAM geochemical analysis laboratory of Aksaray University. The geochemical analysis values of the rocks are presented in Table 3. As a result of the analyses, the CaO values of both natural stones were found to be high and consistent with the thin-section analyses.

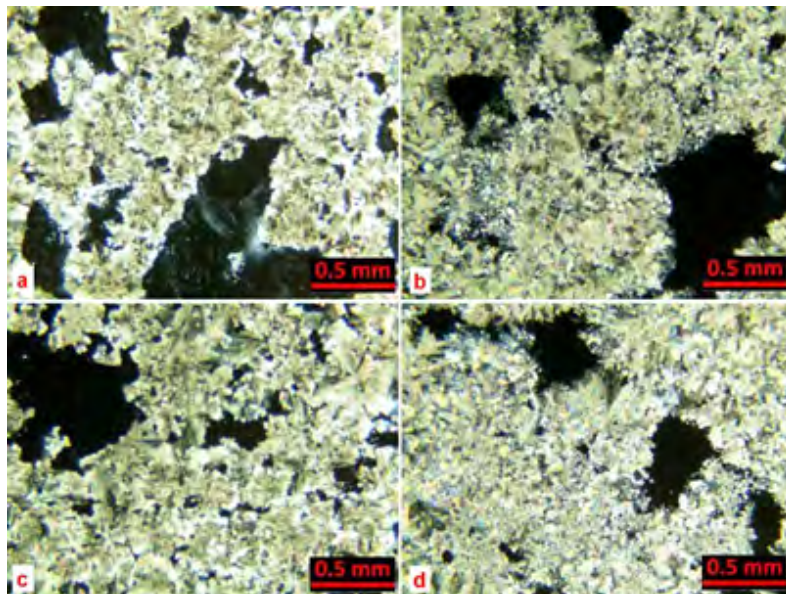


Fig. 6. Thin-section double-nicol images of travertine samples  
a) original sample, b) sample without water-repellent chemical after thermal shock,  
c) sample with solvent-based water-repellent applied, d) sample with water-based water-repellent applied

Rys. 6. Cienkowarstwowe obrazy podwójnego nikolu próbek trawertynu  
a) próbka oryginalna, b) próbka bez środka hydrofobowego po szoku termicznym,  
c) próbka z nałożonym środkiem hydrofobowym na bazie rozpuszczalnika,  
d) próbka z nałożony środek hydrofobowy na bazie wody

Table 3. Chemical analysis results

Tabela 3. Wyniki analizy chemicznej

Chemical content	Limra limestone	Travertine
	%	%
CaO	61.65	60.98
SiO <sub>2</sub>	–	0.06
Fe <sub>2</sub> O <sub>3</sub>	–	0.02
MgO	0.08	0.14
P <sub>2</sub> O <sub>5</sub>	0.03	0.01
MnO	0.02	0.02
LOI	37.75	38.44

## 2.2. Change in the weight of samples dried to constant mass

After the salt-solution thermal-shock experiments, the weight of the samples dried to a constant mass increased. The data obtained is presented in Table 4. The salt solution penetrated the pores of the samples and became saturated. As a result of the evaporation of water during thermal shock, the salts in the solution crystallized in the pores. Therefore, there was an increase in the weight of the samples.

It has been determined that the weight of the samples increase is higher in the samples of limra limestone than in the samples of travertine. The reason for this is that the visible porosity values of limra limestone samples are higher than travertine. Therefore, a higher amount of salt crystallization has occurred in its structure.

Table 4. Average change of weight of samples after thermal shock cycles

Tabela 4. Średnia zmiana masy próbek po cyklach szoku termicznego

Sample code	Average change of weight (%)	Standart deviation	Number of samples
L-O	0.589	0.027	5
L-SO	0.401	0.018	5
L-SB	1.352	0.150	5
TRV-O	0.146	0.009	5
TRV-SO	0.082	0.027	5
TRV-SB	0.141	0.080	5



The mass increase in limra limestone and travertine samples without a water-repellent chemical was higher than in samples with a water-repellent chemical applied. The solvent-based water-repellent chemical has better pore-clogging properties and makes the surfaces more hydrophobic than the water-based one, in both limra limestone and travertine samples. This was observed in the travertine samples taken out of the oven (Figure 7). Figure 7a shows fewer salt crystals around the pores compared to the examples given in Figure 7b and Figure 7c. In Figure 7b, there is salt crystallization all over the surface since there is no chemical applied. In Figure 7c, more salt crystallization was observed than in the example in Figure 7a, but less compared to the example in Figure 7b. The results observed in Figure 8 are also supported by the mass increase values given in Table 4. The colors of salt crystals and limra limestone are similar, so they are not clearly visible in photographs. Therefore, only travertine images are provided.

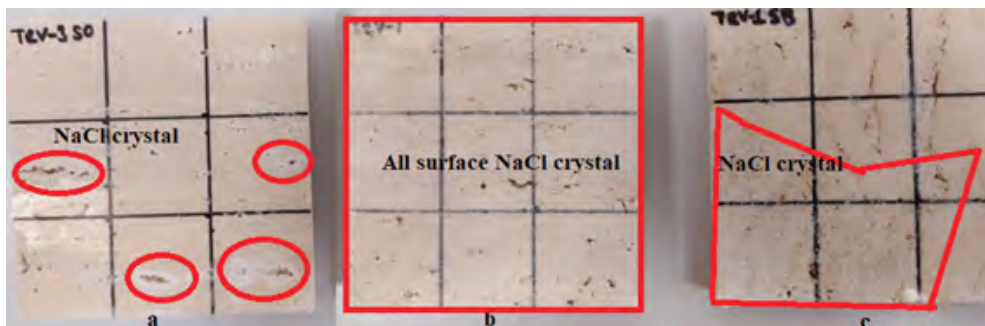


Fig. 7. View of travertine samples after thermal shock cycle  
 a) solvent-based water-repellent chemical applied, b) no water-repellent chemical applied,  
 c) water-based water-repellent chemical applied

Rys. 7. Widok próbek trawertynu po cyklu szoku termicznego  
 a) nałożony środek hydrofobowy na bazie rozpuszczalnika, b) nie nałożony środek chemiczny hydrofobowy,  
 c) nałożony środek chemiczny hydrofobowy na bazie wody

### 2.3. Ultrasound velocity ( $V_p$ ) determination

The determination of ultrasonic velocity ( $V_p$ ) of the samples before and after the thermal shock test was performed according to TS EN 14579 standard using a Proceq device. Sample thicknesses were approximately 20 mm.

When the data obtained after the measurements are examined, a decrease in  $V_p$  rates was observed due to the damage caused by salt crystallization. The highest damage occurred in L-SB samples. The least damage was observed in TRV-SO and L-SO samples. It was observed that water-based water repellent increased the damage in the limra limestone samples. However, it could provide some protection in travertine samples, although not

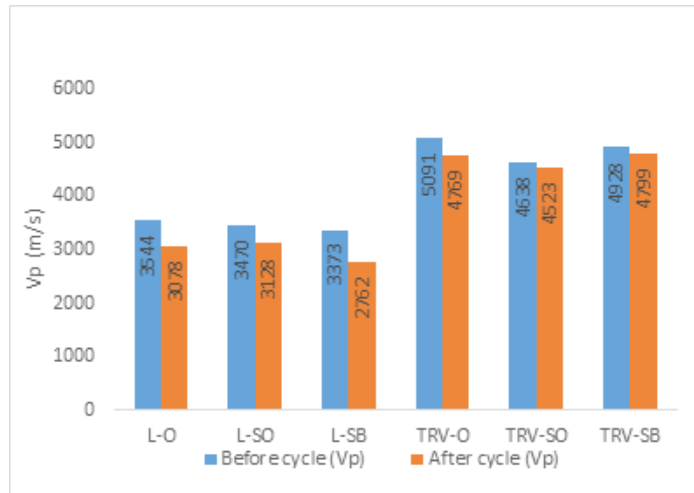


Fig. 8. Ultrasound velocity ( $V_p$ ) changes before and after thermal-shock cycles

Rys. 8. Zmiany prędkości ultradźwięków ( $V_p$ ) przed i po cyklach szoku termicznego

as much as solvent-based water repellent. The changes in the ultrasound velocity ( $V_p$ ) after cycles are given in Figure 8.

## 2.4. Hardness

Hardness is one of the distinguishing features of the minerals that constitute the rock and can be defined as a measure of the resistance of the mineral's surface to scratching or abrasion. Since the rocks are composed of mineral assemblages, the amount of mineral content with a low or high hardness value determines the hardness value of the rock material (Siegesmund and Dürrast 2014).

Leeb hardness as a dynamic hardness testing method, also known as Equotip Leeb hardness, was proposed in the mid-1970s for surface-hardness measurements of metallic materials (Leeb 1979). However, it has also become an increasingly used method for testing materials such as rocks and stones (Wilhelm et al. 2016). This method was developed to offer a faster, more convenient and practical hardness test that can be applied in different test directions with a wider hardness scale (Kompatscher 2004).

Since there is no accepted standard for determining the Leeb hardness of rocks, measurements were conducted on the same samples, taking into account the standard suggested by ISRM (ISRM 2007) for Shore hardness due to the similarity in the measurement methodology.

In order to obtain Leeb hardness (HL) values, 15 readings were made on each sample and the arithmetic averages were calculated after 75 readings in total for each group. When the data obtained after the measurements was examined, a decrease in HL values was ob-

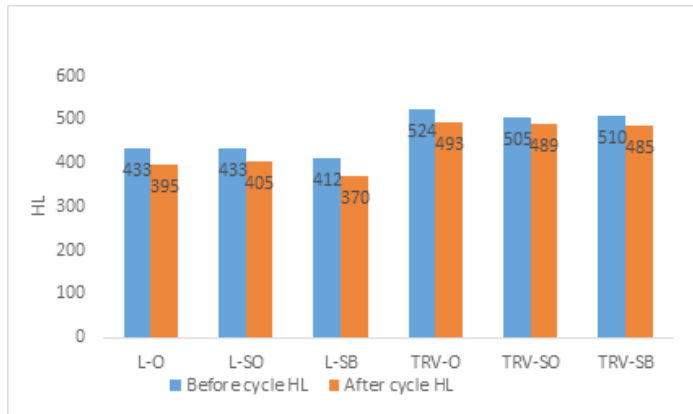


Fig. 9. Leeb hardness (HL) change rates after thermal shock cycles

Rys. 9. Tempo zmian twardości Leeba (HL) po cyklach szoku termicznego

served due to the damage caused by thermal shock and salt crystallization. The highest damage occurred in the L-SB samples, while the least damage was observed in TRV-SO and L-SO samples. It was observed that the water-based water-repellent chemical increased the damage in the limra limestone samples. However, although it was not as effective as the solvent-based water repellent chemical in the travertine samples, it provided some protection. Figure 9 shows the ratio of changes in HL values after cycles.

## 2.5. Color measurement

In today's world, almost all modern color measurements and specifications rely on the system developed by CIE (International Commission on Illumination). In order to provide a more understandable definition of color, CIE introduced a system in 1976, called the CIELab system, which includes three coordinates,  $L^*$ ,  $a^*$ , and  $b^*$ , calculated from X, Y, and Z tristimulus values (Yeşil 2010). The  $L^*a^*b^*$  color model uses rectangular coordinates based on the yellow-blue and green-red axes. The well-balanced structure of the  $L^*a^*b^*$  color space is based on the theory that a color cannot be both green and red or both blue and yellow at the same time (Şahinbaşkan 2002). As a result, simple values can be used to describe the red/green and yellow/blue attributes. When representing a color in CIE  $L^*a^*b^*$ ,  $L^*$  represents lightness ( $L:0$  black,  $L:100$  white),  $a^*$  represents red/green ( $a > 0$  red,  $a < 0$  green), and  $b^*$  represents yellow/blue ( $b > 0$  yellow,  $b < 0$  blue) (Speirs 1998; Brues 2000; Özcan 2008; Eren Sarıcı 2016).

The color difference ( $\Delta E$ ) value is the only method used to quantitatively evaluate the color quality in color measurement. Therefore, there are some limit values for interpreting color-difference values. There is no international standard for these limit values (Öner and

Acar 2006). In short,  $\Delta E^*$  is the measurement of the difference between two colors. It is the distance between the coordinates of two colors (two points on the CIE  $L^*a^*b^*$  color plane). The larger the  $\Delta E$ , the greater the difference between the compared colors. Standard perception intervals for  $\Delta E$  values are given in Table 5. According to the CIE  $L^*a^*b^*$  system, the color difference or distance between two colors is calculated according to Equation 1 (Özcan 2008).

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

$$\Delta L^* = L_1 - L_2,$$

$$\Delta a^* = a_1 - a_2,$$

$$\Delta b^* = b_1 - b_2$$

Table 5. Standard perception intervals in  $\Delta E$  values (Nesapolimer 2022)

Tabela 5. Standardowe przedziały percepcji w wartościach  $\Delta E$

$\Delta E$ (color difference)	Standard Perception	Class
$\leq 1$	Not detectable by the human eye	A1
1–2	Detectable through close observation	A2
2–10	Detectable at a glance	A3
10–49	Colors are more similar than opposite	A4
49–100	Colors are the opposite	A5

Color determination is often used to determine the degree of fading of natural stones before and after aging tests, as well as in the determination of color changes in natural stones with different surface treatments (Sert et al. 2022).

In the scope of the study, water-repellent chemicals were applied to samples of limra limestone and travertine, and color changes were examined after every 5 thermal shock cycles. Lab\* values were determined by conducting 9 measurements on each sample. A PCE-XXM 20 brand color meter was used in the measurements.

As a result of color measurements,  $\Delta L$ ,  $\Delta a$ ,  $\Delta b$  color changes were determined. Color difference values ( $\Delta E$ ) were calculated using Equation 1 according to the obtained values.

In the L-O rock group, a change in the A4 class was observed in the  $\Delta E$  value after the 5<sup>th</sup> cycle. By the 20<sup>th</sup> cycle, the difference between the original color value and the result

had decreased, and it was classified as A3. As a result of thermal shock cycles in L-O samples, the surface wears away, and the original color of the underlying rock appears, causing a decrease in  $\Delta E$  values. In L-SO samples, it was determined that the  $\Delta E$  value was close to the A1 class after solvent-based water repellent application. It was also observed during the examination that the color change was quite low as a result of solvent-based water-repellent chemical application. After thermal shock experiments, the water-repellent surface-protector effect was observed up to the 5th cycle. Although the color difference class was in A2 ( $\Delta E = 1.49$ ), it was determined to be close to the A1 class. Color changes and classes in limra limestone samples (L-O, L-SO, L-SB) after thermal shock cycles are shown in Figure 10.

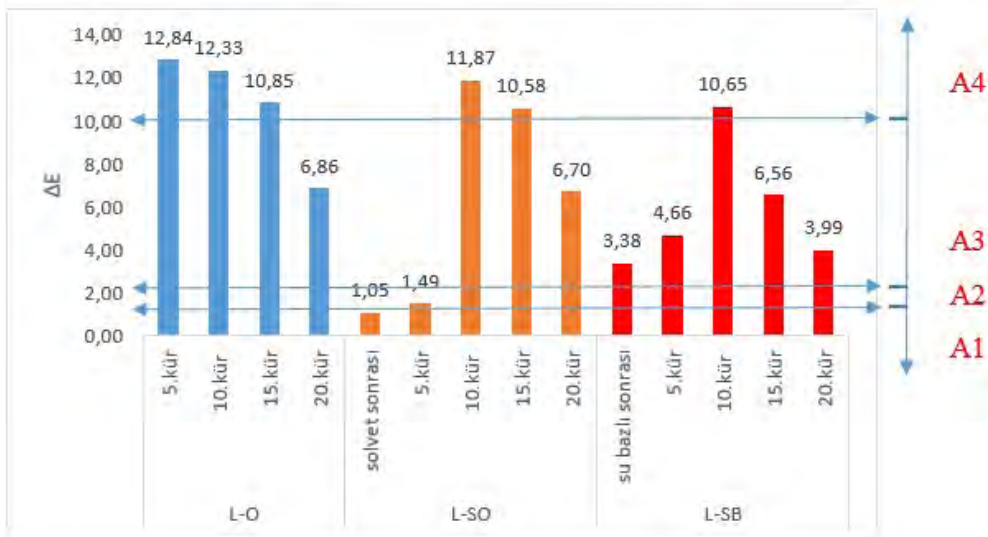


Fig. 10. Color changes and classes in limra limestone samples (L-O, L-SO, L-SB)

Rys. 10. Zmiany barwy i klasy w próbkach wapienia limra (L-O, L-SO, L-SB)

Depending on the rock structure, color changes in travertine samples were lower than those in limra limestone samples. In samples of TRV-O on which no water-repellent chemicals were applied, the color difference increased in the cycle (2.36–3.18–5.14), but a new surface emerged due to wear that occurred on the surface, similar to the limra limestone samples. Therefore, the color-difference value decreased to 2.96. Although the color class of samples treated with solvent-based water-repellent chemicals is A3, it is very close to class A2. No clear color change was observed after the application of water repellent chemicals through visual inspection. No clear color change was observed in TRV-SO samples

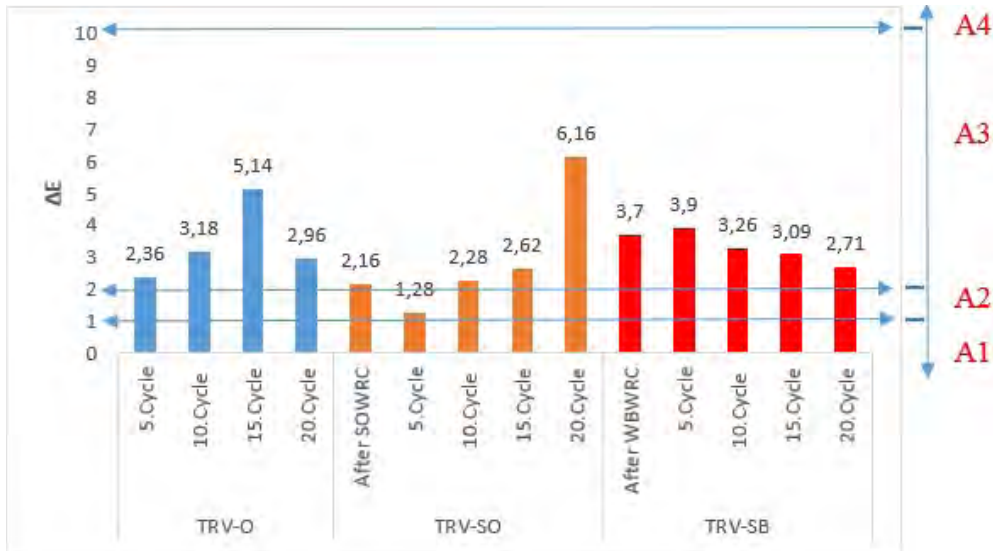


Fig. 11. Color changes and classes in travertine samples (TRV-O, TRV-SO, TRV-SB)

Rys. 11. Zmiany barwy i klasy w próbkach trawertynu (TRV-O, TRV-SO, TRV-SB)

until the 15<sup>th</sup> cycle. However, the color change value increased after the 15<sup>th</sup> cycle (6.16). According to the obtained data, it can be said that the solvent-based water-repellent chemical showed its effect up to the 15<sup>th</sup> cycle. In TRV-SB samples, the color change after applying water-based water-repellent chemicals was higher compared to TRV-SO samples. The color-difference value increased in the 5<sup>th</sup> cycle. However, the difference in color values decreased due to wear that occurred on the surface later. The color changes and classes that occurred in the travertine samples (TRV-O, TRV-SO, TRV-SB) after thermal-shock cycles are shown in Figure 11.

## 2.6. Scanning electron microscopy (SEM) analysis

During the study, water-based and solvent-based water-repellent chemicals were applied to limra limestone and travertine samples, and SEM analyses were performed before and after thermal shock. In addition, EDX analyses were conducted to reveal the effect of salt solution on the water-repellent chemicals after thermal shock. SEM imaging was conducted using the scanning electron microscope (SEM) at the ASÜBTAM laboratory at Aksaray University during the analyses. Prior to the thermal shock experiments, water-repellent chemicals were applied to the limra limestone and travertine samples, and SEM images were taken (Figure 12). After SEM examinations, it was observed that there were smooth surfaces on the samples where water-repellent chemicals were applied.

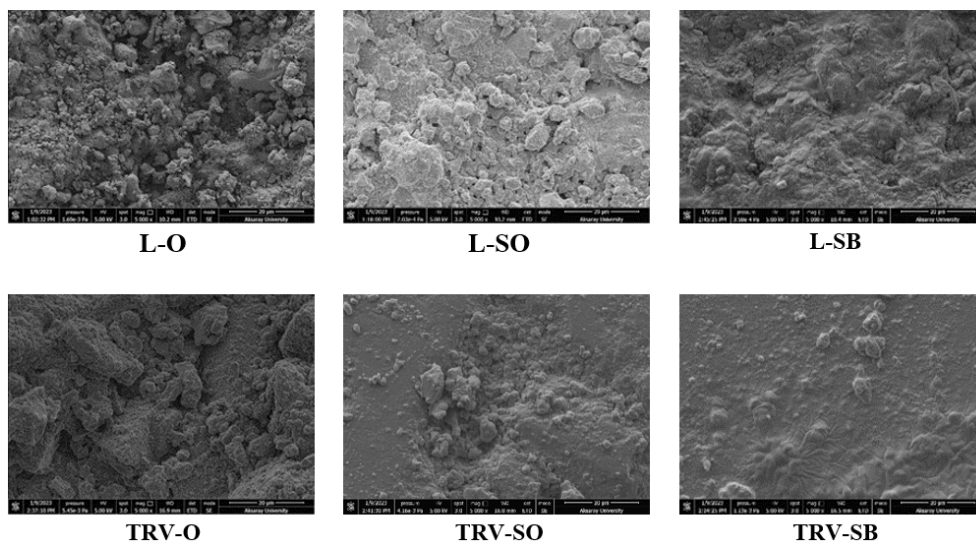


Fig. 12. SEM images of water-repellent and non-water-repellent samples before thermal shock

Rys. 12. Obrazy SEM próbek hydrofobowych i niehydrofobowych przed szokiem termicznym

In the study, SEM analyses were conducted as well as EDX analyses (Figure 13) to detect the micro presence of NaCl crystals on rock surfaces identified macroscopically after thermal shock experiments with salt solution that were performed for 20 cycles. In the EDX analyses, a significant amount of NaCl crystals were observed in the L-O and TRV-O samples on which water-repellent was not applied. In the L-SO and TRV-SO samples on which solvent-based water-repellent chemicals were applied, Na and Cl peaks were lower than in both the samples on which water-repellent was not applied (L-O, TRV-O) and the samples on which water-based water-repellent chemicals were applied (L-SB, TRV-SB). It was observed that the samples treated with water-based water-repellent chemicals lost their hydrophobic property due to the salt effect. This was particularly pronounced in the L-SB sample. In the region where the chemical lost its hydrophobic property, Na and Cl peaks were higher, while in the analysis performed over the water-repellent chemical, Na and Cl peaks were observed to be lower.

### 3. Discussion of results

Especially due to their aesthetic appeal and ease of processing, limra limestone and travertine are preferred as natural building materials, particularly in exterior cladding applications. However, the high water-absorption values of these two natural stones, due to their porosity, make them vulnerable to negative effects from atmospheric conditions.

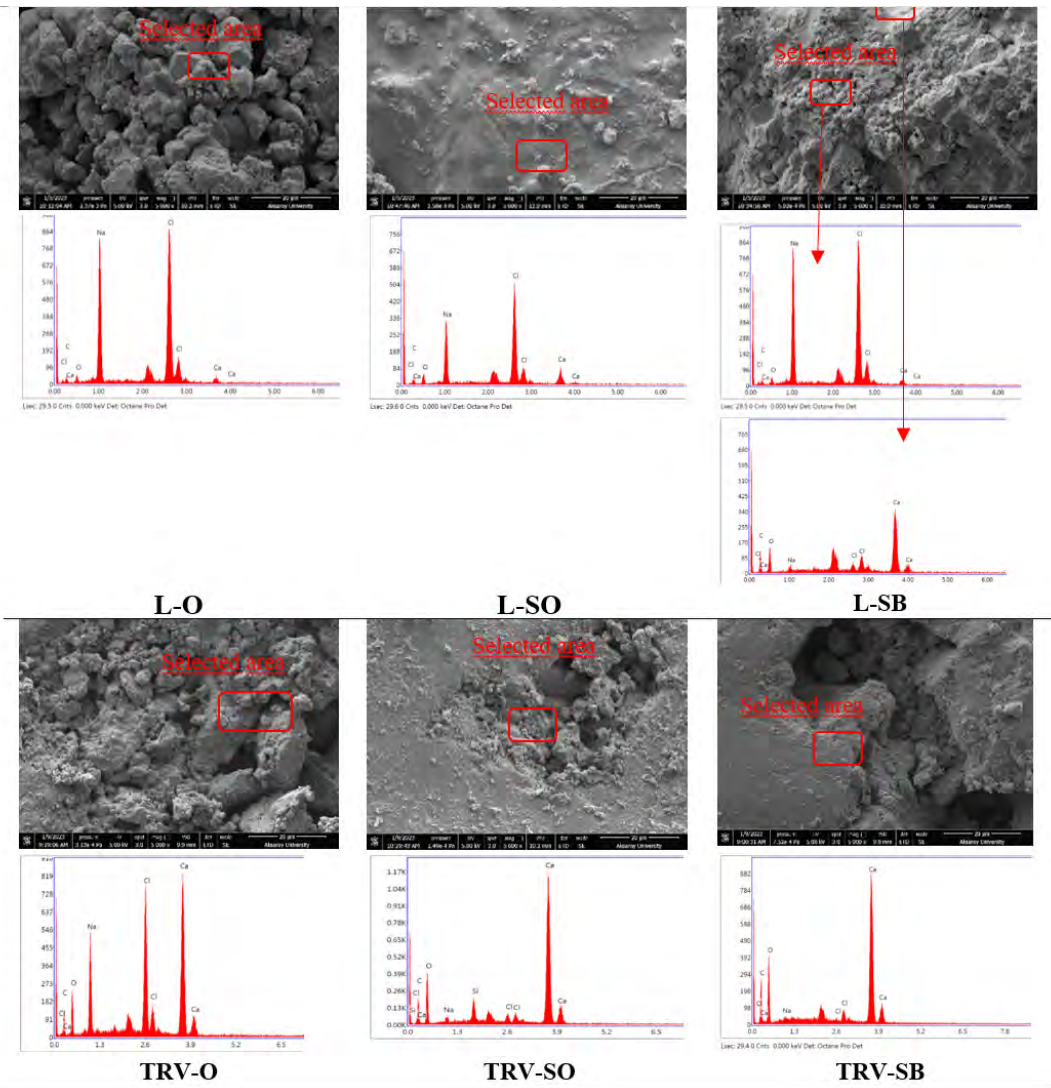


Fig. 13. SEM and EDX images of water-repellent and non-water-repellent samples after thermal shock

Rys. 13. Obrazy SEM i EDX próbek hydrofobowych i niehydrofobowych po szoku termicznym

In this study, two different water-repellent chemicals, one solvent-based and one water-based, were applied on limra limestone and travertine samples. After application, thermal shock tests with a sodium-chloride solution consisting of 20 cycles were performed. The changes in the weights of samples, ultrasonic permeability, Leeb hardness, and color change values in the samples were determined non-destructively after the thermal-shock tests. In addition, the effects of water-repellent chemicals on the formation of NaCl



crystals accumulated in the pores of rocks were also investigated with SEM and EDX analyses. The changes in the non-destructively measured values were compared with the values of reference samples without surface protection. It was found that the solvent-based water-repellent chemical made the surface more hydrophobic than the water-based repellent and delayed the decay resulting from thermal shock and salt crystallization in both natural stone types.

The solvent-based water-repellent chemical delayed the decay in both types of natural stone. However, even the natural stones with surface protection applied undergo erosion over time due to atmospheric conditions. Therefore, the application needs to be renewed at certain intervals.

As a result of thermal shock tests, limra limestone samples were adversely affected by the crystals formed by the dissolved salt it absorbed, in addition to thermal expansion and contraction compared to travertine samples.

There were changes in the direction of decreasing ultrasonic-velocity values after thermal-shock cycles. The lowest change was observed in the samples of both natural stone types where solvent-based water-repellent chemical was applied.

The HL hardness value is related to many mechanical properties. Therefore, in this study, it has provided an idea about the decay that occurs in rocks due to atmospheric conditions. In long-term examinations, it has been determined that HL values can be used non-destructively. As with the results of ultrasonic velocity changes, the lowest changes in HL values were observed in the samples where the solvent-based water-repellent chemical was applied.

Color determinations are conducted before and after aging tests to determine color changes in natural stones. In the study, the color change values were found to be lower for both types of natural stones used after solvent-based water-repellent application compared to water-based water-repellent chemical.

Light-colored and porous stones such as limra limestone and travertine provide natural climate control in the environment, especially as they reflect more sunlight. Due to these properties, they are frequently used in hot and seaside areas. The application of water repellent chemicals to the surfaces of these stones results in longer-lasting external facades in hot and seaside areas and a significant decrease in color changes that may occur over time, making them indistinguishable in macroscopic observations.

Before applying water repellent chemicals, the properties of the individual agent should be taken into account in relation to the geochemical and other engineering properties of the natural stone. Otherwise, irreversible damage may occur on the applied surface.

In this study, water-repellent chemicals were applied to the entire surface of the samples. However, in the areas where the application is planned, especially in the rocks used as base flooring, even though it has a protective property, it will not be able to prevent water from penetrating into the structure from the bottom. It would be more appropriate to apply the water-repellent chemical to the rocks used as exterior cladding, where it is more effective in preventing water penetration.

## REFERENCES

- Akbay et al. 2012 – Akbay, D., Efe, T., Şengün, N., Demirdağ, S., Altındağ, R. and Erinc Koççaz, C. 2012. Investigation of freezing-thawing and thermal shock effects on various marble. MERSEM'2012 8. *International Marble and Natural Stone Congress*, 13–15.
- Bromblet, P. and Martinet, G. 2002. Joints, mortiers de pose et produits de ragréage: Les différentes pathologies: Réflexions et préconisations. *Pierre actual: Matériaux, ouvrages, techniques* 785, 66–79.
- Brues, S. 2000. "Postscriptum on Color Management" GretagMacbeth, Switzerland.
- Butler, T.J. and Likens, G.E. 2019. *Acid rain, pollution*. [Online:] <https://www.britannica.com/science/acidrain/Effects-on-human-made-structures> [Accessed: 2022-12-15].
- Cetin, C. 1998. *Providing water impermeability of marbles with silicate solutions*. Master's thesis, Süleyman Demirel University, Institute of Science and Technology, Isparta.
- Charola, A.E. 1995. Water-repellent Treatments for Building Stones: A practical over-view. *APT Bulletin* 26(2–3), 10–17, DOI: 10.2307/1504480.
- Coussy, O. 2006. Deformation and stress from in-pore drying-induced crystallization of salt. *Journal of the Mechanics and Physics of Solids* 54(8), 1517–1547, DOI: 10.1016/j.jmps.2006.03.002.
- Çelik et al. 2018 – Çelik, M.Y., Ersoy, M., Arsoy, Z., Sert, M. and Yeşilkaya, L. 2018. Investigation of the effect of water repellent chemicals on the weathering of İncehisar andesites due to salt crystallization. *Scientific Mining Journal* 57(2), 81–94.
- Çelik et al. 2019 – Çelik, M.Y., Sert, M. and Arsoy, Z. 2019. Investigation of the effect of surface protective resin on capillary water absorption potential of Döğür tuff and İncehisar andesite. *Uludağ University Journal of Engineering Faculty* 24(3), 319–338, DOI: 10.17482/uumfd.476527.
- Derluyn et al. 2014 – Derluyn, H., Moonen, P. and Carmeliet, J. 2014. Deformation and damage due to drying induced salt crystallization in porous limestone. *Journal of the Mechanics and Physics of Solids* 63, 242–255, DOI: 10.1016/j.jmps.2013.09.005.
- Erdoğan, Y. and Yaşar, E. 2001. *Evaluation of Adana-Icel Osmaniye marbles in terms of engineering properties*. Turkey Marble Symposium (Mersem 2001) Proceedings Book, pp. 163–174, Afyon.
- Eren Sarıcı D. 2016. Thermal deterioration of marbles: Gloss, color changes. *Construction and Building Materials* 102, 416–421, DOI: 10.1016/j.conbuildmat.2015.10.200.
- Ersen et al. 2013 – Ersen, A., Verdön, İ. and Pekmezci, İ.P. 2013. Surface protectors and titanium dioxide surface coating method the effect of nano-technological surface protector application on limestone surfaces on the physical properties of the stone and protection against pollution. *Journal of Restoration and Conservation Studies* 11, 37–48.
- Ioannou, I. and Hoff, W.D. 2008. Water repellent influence on salt crystallisation in masonry. *Proceedings of the Institution of Civil Engineers – Construction Materials*, 161, 17–23.
- ISRM 2007. *Rock Characterization, Testing and Monitoring – ISRM Suggested Methods*. Brown, E.T. (ed.), Pergamon Press, 211 pp.
- Kılıç, İ. and Gültekin, A.H. 2009. Effects of surface protection resin on water absorption and strength of sandstone. *5<sup>th</sup> International Advanced Technologies Symposium*, Karabük University, 2196–2199.
- Kompatscher, M. 2004. Equotip – rebound hardness testing after D. Leeb. [In:] *Conference on hardness measurements theory and application in laboratories and industries*, pp. 66–72.
- Leeb, D. 1979. Dynamic hardness testing of metallic materials. *NDT Int* 12(6), 274–278.
- Licchelli et al. 2013 – Licchelli, M., Malagodi, M., Weththimuni, M.L. and Zanchi, C. 2013. Water-repellent properties of fluoro elastomers on a very porous stone. Effect of the application procedure. *Progress in Organic Coatings* 76, 495–503, DOI: 10.1016/j.porgcoat.2019.04.006.
- Nesapolimer 2022. [Online:] <https://nesapolimer.com.tr/renk-olcumu-nedir/> [Accessed: 2022-09-21] (in Turkish).
- Öner, E. and Acar, K. 2006. Color measurement in textile industry, Seminar Notes, Adana.
- Özcan, A. 2008. The determination of rough paper surface effect on L\*a\*b\* values. *Istanbul Commerce University Journal of Science* 7(14), 53–61.
- Pérez et al. 2014 – Pérez, N.A., Lima, E., Bosch, P. and Méndez-Vivar, J. 2014. Consolidating materials for the volcanic tuff in western Mexico, *Journal of Cultural Heritage* 15, 352–358, DOI: 10.1016/j.culher.2013.07.010.

- Pinna et al. 2011 – Pinna, D. Salvadori, B., Porcinai, S. 2011. Evaluation of the application conditions of artificial protection treatments on salt-laden limestones and marble. *Construction and Building Materials* 25(5), 2723–2732, DOI: 10.1016/j.conbuildmat.2010.12.023.
- Sert et al. 2022 – Sert, M., Ekincioglu, G. and Akbay, D. 2022. *Methods applied in the selection of natural stones used in the building sector*. Industrial Raw Materials in the Building Sector, Serhan Haner, Editor, İksad Publishing House, Ankara, 127–160.
- Siegesmund, S. and Dürrast, H. 2014. *Physical and mechanical properties of rocks*. Siegesmund, S. and Snethlage, R. (eds). Stone in architecture, properties, durability, Springer, Berlin.
- Speirs, H. 1998. Introduction to prepress, BPIF, Pira International, UK. The Basic Principles of Color and Lab for Computer Publishing (2003), Linotype-Hell.
- Şahinbaşkan, T. 2002. *Determining Color Separation Parameters in Desktop Publishing*. Marmara University, Institute of Science and Technology, Department of Printing Education, PhD Thesis, 227s, Istanbul.
- TEKNO Construction Chemicals Catalog. [Online:] <https://teknoyapi.com.tr/documents/TDS-teknosil-w.pdf> [Accessed: 2022-06-05].
- Thaulow, N. and Sahu, S. 2004. Mechanism of concrete deterioration due to salt crystallization. *Mater Charact* 53, 123–127, DOI: 10.1016/j.conbuildmat.2014.06.011.
- Thomachot-Schneider et al. 2011 – Thomachot-Schneider, C., Gommeaux, M., Fronteau, G., Oguchi, C.T., Eyssautier, S. and Kartheuser, B. 2011. A comparison of the properties and salt weathering susceptibility of natural and reconstituted stones of the Orval Abbey (Belgium). *Environmental Earth Sciences* 63, 1447–1461, DOI: 10.1007/s12665-010-0743-8.
- TS EN 14066 – 2015. *Natural Stones – Test Methods – With thermal shock effect determination of wear resistance*. Turkish Standards Institute, Ankara.
- TS EN 14579 – 2006. *Natural Stones – Experimental Methods – Determination of sound speed progression*. Turkish Standards Institute, Ankara.
- Tulliani et al. 2014 – Tulliani, J.M., Serra, C.L. and Sangermano, M. 2014. A visible and long-wavelength photo-cured epoxy coating for stone protection. *Journal of Cultural Heritage* 15, 250–257, DOI: 10.1016/j.culher.
- Vallet et al. 2000 – Vallet, J.M., Bromblet, P., Vergès-Belmin, V., Pallot-Fossard, I. and Henry, F. 2000. La protection des pierres: Guide sur le shydrofuges de surface. Les cahiers techniques du cercle des partenaires du patrimoine 3. Champs-sur-Marne: Cercle des partenaires du patrimoine.
- Wilhelm et al. 2016 – Wilhelm, K., Viles, H. and Burke, O. 2016. Low impact surface hardness testing (Equotip) on porous surfaces – advances in methodology with implications for rock weathering and stone deterioration research. *Earth Surface Processes and Landforms* 41(8), 1027–1038, DOI: 10.1002/esp.3882.
- Yeşilay, S. 2019. A Review On the Dense Hydroxyapatite Coating Films On Marble. *Izlek Academical Journal* 2(1), 1–11.
- Yeşil, Y. 2010. *Estimation of Color Values in Melange Fiber Blends by Developing a New Algorithm*. Çukurova University Institute of Science and Technology, Department of Textile Engineering (Doctoral dissertation, PhD thesis, Adana).

**NON-DESTRUCTIVE METHODS DETERMINATION OF THERMAL SHOCK  
RESISTANCE OF NATURAL BUILDING STONES APPLICATED WITH DIFFERENT  
WATER REPELLENT CHEMICALS ON THEIR SURFACES**

**Keywords**

natural stone, water-repellent chemical, thermal shock, color analysis, Leeb hardness

**Abstract**

Natural stones are used as coating material on the exteriors and terraces of buildings in architecture, and in places such as entrances, halls, living rooms, kitchens, bathrooms and stairs in interior spaces. Limra limestone and travertine are used as natural building materials in many structures depending on their colors. However, the water absorption values of these two natural stones are high due to their porosity, resulting in negative effects from atmospheric conditions. In this study, two different carbonate-based natural stones, limra limestone and travertine, were treated with two different water-repellent chemicals, one solvent-based and one water-based. After application, thermal shock tests were performed with a sodium chloride solution consisting of twenty cycles. The changes in the weights of samples dried to constant mass, ultrasonic permeability, Leeb hardness, and color change values in the samples were determined after the thermal shock tests. In addition, the effects of water-repellent chemicals on the formation of NaCl crystals accumulated in the pores of the rocks were examined by SEM and EDX analysis. Changes in non-destructively measured values were compared with the values of reference samples without surface protection. The solvent-based water-repellent chemical made the sample surface more hydrophobic than the water-based repellent. In both types of natural stones, the solvent-based water repellent chemical showed more protective properties against salt crystallization under thermal shock conditions compared to the water-based repellent.

**METODY NIENISZCZĄCE OZNACZANIA ODPORNOŚCI NA SZOK TERMICZNY  
NATURALNYCH KAMIENI BUDOWLANYCH NAKŁADANYCH  
NA ICH POWIERZCHNIE RÓŻNYMI ŚRODKAMI HYDROFOBOWYMI**

**Słowa kluczowe**

kamień naturalny, środek hydrofobowy, szok termiczny, analiza barwy, twardość Leebea

**Streszczenie**

Kamienie naturalne są stosowane jako materiał powłokowy na zewnątrz i tarasach budynków w architekturze oraz w miejscach takich jak wejścia, hole, pokoje dzienne, kuchnie, łazienki i schody w przestrzeniach wewnętrznych. Wapień limra i trawertyn są wykorzystywane jako naturalne materiały budowlane w wielu konstrukcjach w zależności od ich kolorystyki. Jednak wartości nasiąkliwości tych dwóch kamieni naturalnych są wysokie ze względu na ich porowatość, co skutkuje

negatywnym oddziaływaniem warunków atmosferycznych. W tym badaniu dwa różne kamienie naturalne na bazie węglanów, wapień limra i trawertyn, potraktowano dwoma różnymi hydrofobowymi chemikaliami, jednym na bazie rozpuszczalnika i jednym na bazie wody. Po aplikacji przeprowadzono testy szoku termicznego z roztworem chlorku sodu składające się z 20 cykli. Zmiany masy suszonych do stałej masy próbek, przepuszczalność ultradźwięków, twardość Leebea oraz zmiany barwy w próbkach określono po testach szoku termicznego. Ponadto zbadano wpływ chemikaliów hydrofobowych na powstawanie kryształów NaCl gromadzących się w porach skał za pomocą analizy SEM (skaningowa mikroskopia elektronowa) i EDX (rentgenowska dyspersja energii). Zmiany wartości mierzonych w sposób nieniszczący porównano z wartościami próbek referencyjnych bez zabezpieczenia powierzchni. Środek hydrofobowy na bazie rozpuszczalnika sprawił, że powierzchnia próbki była bardziej hydrofobowa niż powierzchnia na bazie wody. W obu typach kamieni naturalnych hydrofobowa substancja chemiczna na bazie rozpuszczalnika wykazywała lepsze właściwości ochronne przed krystalizacją soli w warunkach szoku termicznego w porównaniu z substancją na bazie wody.

