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ORIGINAL PAPER

# A preliminary study on the conservation and polishing performance of Sanliurfa limestones as a traditional building material

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**Abstract** Sanliurfa limestones have been used as building materials from antiquity to current day (e.g., Gobeklitepe temple B.P. 14,000, Bazda underground quarries B.P. 3000, Harran castle B.P. 3000, etc.). These antique structures are listed within the United Nations Educational, Scientific and Cultural Organization (UNESCO)'s World Heritage List. However, the stones were used in these structures without any protection, and atmospheric conditions (precipitation, acid rain, temperature changes, etc.) cause damage to these stones over time, such as strength loss, abrasion, and discoloring. The damage can lead to the collapse of precious historical structures, or may require costly restoration. In this study, Sanliurfa limestone was investigated with respect to conservation using polish insulation (polysiloxane, lithium silicate, and varnish), appearance performance by polishing, and potential usage in the marble industry. The results revealed that conservatives could maintain up to 92 % of the unconfined compressive strength (UCS) of the natural stone and reduced acid abrasion to 0.5 % of the original weight. The stone gained a bright appearance after polishing, especially by lithium silicate. Thus, it can be stated that it is possible to recover or prolong the lifetime of the monuments that were constructed using Sanliurfa limestone, and this limestone may have great industrial potential as marble stone.

**Keywords** Limestone · Water absorption · Strength · Stone conservation · Polishing · Sanliurfa (Turkey)

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## Introduction

Sanliurfa has been a land for settlement for various civilizations since B.P. 14,000. Prior to the use of reinforced concrete structures, Sanliurfa limestone (SLS) was the main building material, due to its high strength and the high insulation properties. SLS can easily be cut with a hand-held saw or a rock-cutting machine, and is suitable for building masonry walls. SLS has been widely used in historic structure. However, SLS tends to absorb water, and this has an impact upon its physical and mechanical properties. Water absorption is triggered by precipitation and by surface runoff. It has been well established that the most damaging component of atmospheric conditions on building stones is precipitation, as water saturation decreases the strength of the stones, acid rain shortens the life of the stones by abrasion, and discoloration (yellowing, darkening, etc.) resulting from the precipitation impacts not only affects the aesthetic appearance, but may also result in physical damage to the stone (Winkler 1973; Azzoni et al. 1996; Singh et al. 1999; Sharma et al. 2007; Ozcelik and Ozguven 2014). Turgut et al. (2008), Kulaksiz and Agan (2009), Agan (2011), and Agan et al. (2013) state that SLS loses its strength by 25–60 % under saturated conditions. As a result, SLS can lose its strength over time, and this situation can lead to the collapse of these cultural heritage monuments (Kaufmann and Quinif 1999; Devos et al. 2005) or can cause costly (Sariisik and Sariisik 2011; Bednarik et al. 2014) and incompatible restorations (Zezza 1990; Bernd and Kurt 2005; Fronteau et al. 2010). Overall, moisture susceptibility affects the lifetime of existing structures built with SLS, and adversely affects the future use of SLS as a building material.

The ageing and decay processes of monuments have accelerated in recent decades due to atmospheric pollution and acid rain, and therefore, conservation has become a focus of research in many fields (Striegel et al. 2003). Fossil fuels, which have been widely used in recent decades due to increasing industrialization and urbanization, generate corrosive gases (e.g., $CO_2$). These gases play a major role in air pollution and the formation of acid rain. In acid rain, the primary contributors are hydrogen ions, in addition to natural sources of acidity, such as sulfurous ($SO_x$) and nitrous ($NO_x$), which convert to sulfuric acid ($H_2SO_4$) and nitric acid ($HNO_3$) in a reaction with water, lowering the pH of the rain and accelerating the weathering processes of all carbonate materials (Sharma et al. 2007). The pH of the rain in polluted areas is generally 4–5. Consequently, there is a need to investigate the conservation methods of SLS against atmospheric conditions, to prolong the lifetime of monuments with consideration to the high variability of the response of natural stones to the treatment methods. With appropriate treatment, stone would not lose its strength and original appearance, the structures would withstand weathering processes for a long time, and the use of SLS in new construction would be feasible.

Several studies on geotechnical properties of SLS are available in the literature (Canakci et al. 2007; Turgut et al. 2008; Kulaksiz and Agan 2009; Agan 2011; Agan et al. 2013). However, these investigations were performed specifically to obtain geological and geotechnical data on SLS, and generally were not related to polishing performance or to the determination of conservation alternatives for SLS. No studies were identified in the literature where conservatives were used to treat SLS. This study was conducted to eliminate this gap in the literature, as well as to provide guidance to the natural stone industry.

The objectives of this study were (1) to determine the effect of water on strength of SLS, (2) to determine the maximum unconfined compressive strength (UCS) of SLS resulting from the use of various treatment methods, (3) to determine the performance of polish on SLS, and (4) to examine the potential usage of SLS as building stone. To attain the objectives of the study, SLS were subjected to UCS tests (under natural, dried, saturated, fire damaged and freeze–thaw cycled conditions), water absorption by weight tests, resistance to acid abrasion tests, and abrasion and discoloration observations by a microscope. The test conditions were established using observations provided in the literature. For example, Sariisik (1998) and Neville (2000) state that concrete can lose its strength due to fire exposure. Also, Gomez-Heras et al. (2009), Lam dos Santos et al. (2011), Ozguven and Ozcelik (2013), Brotons et al. (2013), and Ozguven and Ozcelik (2014) determined that natural stones can lose their strength as a function of temperature. The processes that resulted in maximum UCS and provided insulation of SLS from water, atmospheric conditions, and acid rain were investigated using three types of industrial polish (polysiloxane, lithium silicate and varnish). In addition, the effects of polishing on SLS, the effectiveness of the specific selected polishes (polysiloxane and lithium silicate) that indicated the best and the brightest appearance, and the potential usability of SLS as a substitute for marble were examined.

## Site information and geological characteristics of SLS

SLS is encountered in a large area that extends over 18,500 km$^2$ in South-East Anatolia in Turkey (Fig. 1). The dominant geological unit in the area is Miocene-Eocene limestone. During tectonic activities, horst and graben formations occurred in the region. The graben parts of these tectonic formations had become a stack deposit of Quaternary Clay. These deposits formed the agricultural Sanliurfa, Ceylanpinar, Harran, Siverek, Suruc, Hilvan, and Bozova plains. The Sanliurfa plains have an average altitude of 520 meters above sea level, and are covered by almost horizontally layered clay. Quaternary Clay is generally above the Miocene-Eocene limestone, having a thickness of several hundred meters, and/or above the Plio Quaternary volcanic basalt, having a thickness of several meters (Turgut et al. 2008; Kulaksiz and Agan 2009; Agan 2011; Agan et al. 2013). Miocene-Eocene limestones are exposed on the surface of the hills all over the region. The origin of the Plio Quaternary basalts is the volcanic Karacadag mountain, which is located 120 km northeast of the city of Sanliurfa. Basalts appear on the surface of some hills, especially in the north of the study area (Yesilnacar and Cetin 2005). SLS referred to as the Sanliurfa Formation (Canakci et al. 2007) surround the Sanliurfa city center and the Harran plain. In all these regions, limestones were extracted, either from an open pit or from underground quarries.

Turgut et al. (2008) performed chemical analysis of the SLS using atomic absorption spectrometry. The results are

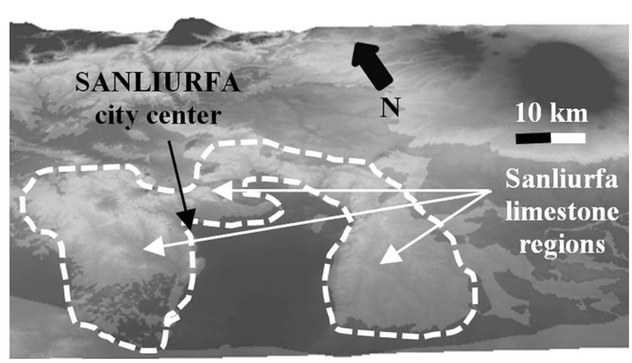


**Fig. 1** Satellite map of Sanliurfa and limestone regions

given in Table 1. They show that the SLS have a very high content of $CaCO_3$. Agan et al. (2013) performed thin-sections of four samples collected from different quarries. Thin-section studies indicated that all samples were micritic or micro-sparitic or sparitic limestones, and included abundant amount of calcite mineral with some fossils. In addition, X-ray diffraction analyses of these samples were also conducted. The XRD diffractograms showed that calcite was the dominant mineral in the limestone samples. However, in two samples, small amounts of dolomite were also observed.

SLS can easily be cut with a hand-held saw or a rock-cutting machine, and therefore is suitable for building masonry walls. The processing of the SLS can be adversely affected by the presence of contaminants such as argillaceous, chalk, and chert within the SLS. Samples of stones used for construction have been obtained from new quarries (Fig. 2a), ancient open pits (Fig. 2b), and ancient underground quarries (Fig. 2c). There are more than 300 small underground caverns and quarries in Sanliurfa. Some of these are located down to a depth 10 m below the surface, and they sometimes have up to four levels. Most of the self-supported caverns are used during the hot summer season as a places for food storage (Fig. 2b) as well as barns for animals (Fig. 2c). The physico-thermal properties of the SLS are tabulated in Table 2. The rather high porosity (around 17 %) must be noticed.

**Table 1** Chemical constituents of the SLS (Turgut et al. 2008)

| Chemical constituent | Mean values (%) |
|---|---|
| CaO | 54.69 ± 0.10 |
| Loss on ignition | 43.33 ± 0.46 |
| Undefined | 0.54 ± 0.23 |
| $SiO_2$ | 0.50 ± 0.10 |
| MgO | 0.44 ± 0.06 |
| $Al_2O_3$ | 0.29 ± 0.02 |
| $Fe_2O_3$ | 0.20 ± 0.04 |
| Total | 99.46 |

Prior to the use of reinforced concrete structures, SLS was the main building material for decoration (Fig. 3a), major construction (Fig. 3b), fountain construction (Fig. 3c) and external cladding (Fig. 3d). Furthermore, SLS was used in the area for art by stone craftsmen, e.g., see Gobeklitepe (Fig. 3e), the oldest antic temple discovered (14,000 years B.P.), stone relief sculptures and catacombs in Gobeklitepe (Fig. 3f), Orpheus (Fig. 3g) mosaic (1820 years B.P.), and Balikligol (Fig. 3h) the first and the oldest full-sized human statue discovered (13,500 years B.P.). The rock mass classifications of the SLS are tabulated in Table 3.

In addition to accessibility and ease of quarrying, SLS has good isolation and strength properties. However, SLS tends to absorb water and as seen from the historical structures, major stone erosion occurs in the roof and base of the masonry walls. The decomposition of materials occurs due to precipitation for the roofs of the masonry walls, and due to surface runoff for the bases. The best-preserved stones are observed in the middle parts of the walls (Fig. 4a–d). The mechanical properties of the SLS are tabulated in Table 4.

The Sanliurfa and the Harran Castles have been restored, 3000 years after their initial construction, to their original functions. However, obtaining the original color and appearance was impossible (Fig. 4g, h). Also, the strength of stones may be altered by the natural ageing of the stone. In addition, the quality of the stones may vary between quarries (Nicholson 2000; Cardell et al. 2003).

Susceptibility to moisture and natural variations also adversely affect the potential use of SLS for new construction. Therefore, detail investigations were needed to explore alternatives to prevent the SLS from atmospheric conditions.


**Fig. 2** Photographs of (**a**) new, (**b**) ancient open air, and (**c**) ancient underground quarries

**Table 2** Physico-thermal properties of the SLS

| Material properties | Turgut et al. (2008) | Agan (2011) | Agan et al. (2013) |
|---|---|---|---|
| Dry unit weight (kN $m^{-3}$) | 20.8 ± 0.80 | 20.60 | 17.5 ± 0.80 |
| Saturated unit weight (kN $m^{-3}$) | 22.5 ± 0.40 | – | 20.2 ± 0.70 |
| Specific gravity | – | – | 2.64 ± 0.04 |
| Density (gr $cm^{-3}$) | 2.57 ± 0.00 | – | – |
| Void ratio (%) | 19.2 ± 3.10 | – | – |
| Absorption by weight (%) | 8.4 ± 2.50 | – | 15.0 ± 1.10 |
| Porosity (%) | 17.2 ± 4.30 | – | 25.4 ± 3.90 |
| Mass loss after freeze–thaw (%) | 0.07 ± 0.01 | – | – |
| Thermal conductivity (W $m^{-1}$ $K^{-1}$) | 1.42 ± 0.09 | 0.91 | – |
| Specific heat (J $kg^{-1}$ $C^{-1}$) | 1,041 ± 0.94 | – | – |
| Thermal diffusity ($m^2$ $s^{-1}$ $10^{-7}$) | 6.64 ± 0.98 | – | – |
| Dry P-wave velocity (km $s^{-1}$) | 3.27 ± 0.24 | – | 2.72 ± 1.10 |
| Saturated P-wave velocity (km $s^{-1}$) | – | – | 2.53 ± 5.10 |
| Dry S-wave velocity (km $s^{-1}$) | – | – | 1.42 ± 1.70 |
| Saturated S-wave velocity (km $s^{-1}$) | – | – | 1.17 ± 5.00 |

**Fig. 3** Examples of uses of SLS for (**a**) decoration, (**b**) construction, (**c**) fountain, (**d**) external cladding, (**e**) temple, (**f**) stone relief sculpture, (**g**) mosaic, and (**h**) statue

**Table 3** Rock mass classifications of the SLS

| Condition of the SLS | Kulaksiz and Aydan (2010) | | Agan et al. (2013) |
|---|---|---|---|
| | RMR | Q | |
| Massive | 80–90 | 5–50 | 77–82 |
| Thickly bedded | 60–80 | 5–25 | 64–74 |
| Thinly bedded | – | – | 59–69 |


**Fig. 4** Photographic evidence of (**a–d**) stone erosion that occurred on the roofs and in the bases of the masonry walls, (**e–f**) the structural damage, and (**g–h**) incompatible restorations

**Table 4** Mechanical properties of the SLS

| Material properties | Turgut et al. (2008) | Agan (2011) | Agan et al. (2013) |
|---|---|---|---|
| Dry compressive strength, UCS (MPa) | 17.8 ± 1.70 | 15 | 15.62 ± 2.40 |
| Saturated compressive strength (MPa) | 14.7 ± 2.20 | – | 14.10 ± 1.21 |
| Dry Brazilian tensile strength (MPa) | – | – | 1.83 ± 0.21 |
| Saturated Brazilian tensile strength (MPa) | – | – | 0.81 ± 0.09 |
| Dry bending strength (MPa) | – | – | 3.77 ± 0.56 |
| Saturated bending strength (MPa) | – | – | 1.47 ± 0.19 |
| Dry UCS after freeze–thaw (MPa) | 16.3 ± 1.20 | – | – |
| Saturated UCS after freeze–thaw (MPa) | 12.7 ± 1.30 | – | – |
| Dry Schmidt rebound (MPa) | 21 ± 2 | – | – |
| Saturated Schmidt rebound (MPa) | 16 ± 2 | – | 12.6 ± 0.60 |
| Modulus of elasticity (GPa) | 13.9 ± 2.60 | 18 | 13.1 ± 3.50 |
| Poisson's ratio | 0.31 ± 0.03 | 0.24 | 0.22 ± 0.03 |
| Slake durability index $Id_2$ (%) | – | – | 87.5 ± 2.80 |

## Methodology

An extensive testing program was conducted to assess the water absorption and strength properties of SLS. The testing program consisted of unconfined compressive strength (UCS) tests, water absorption tests, acid abrasion tests and microscopic analysis. The testing program was conducted on samples that were natural; saturated; dried; exposed to freeze–thaw cycles; exposed to fire cycles; treated by conservatives and then saturated; and samples that were initially dried and then treated by conservatives, and finally saturated samples.

Initially, UCS tests were conducted to evaluate the influence of water content on compressive strength. The UCS tests were conducted on the SLS samples under natural, dried, and fully saturated conditions. A total of 165 UCS tests and 70 water absorption tests were conducted. In UCS tests, 15 samples were tested in their natural state, 15 samples were tested after immersion in water for 7 days, and 15 samples were tested after drying in an oven at 105 °C for 3 days. The UCS and the water absorption properties of the samples were determined. Additionally, in order to examine the probable adverse effects of fire on the strength of the SLS, 15 samples were placed in a 600 °C wood-burning oven with open flames for 3 days. Fire exposure time was selected in accordance with Sariisik (1998) and Sariisik et al. (2005). Then, the UCS values of the fire-exposed samples were determined, and compared with the UCS values of the natural samples. Furthermore, in order to examine the probable adverse effects of freeze–thaw on the strength of the SLS, 15 samples were subjected to three freeze–thaw cycles in accordance with ASTM D5312 M-12 (2013). Then, the UCS values of the freeze–thaw-exposed samples were determined, and compared with the UCS values of the natural samples. Experimental samples were obtained from a commercial quarry, and


**Fig. 5** Natural and treated samples for HCl acid tests

prepared as cubes with dimensions of150 ± 10 mm, following ASTM C170 (1999). UCS and water absorption tests were carried out in accordance with the ASTM C170 (1999) and ASTM C97 (1996) standards, respectively.

Next, in order to examine the effect of polishing with water-repellent treatment on stone conservation, a total of 75 natural samples were treated by three types of industrial polish. A total of 25 samples was treated by polysiloxane, 25 samples by lithium silicate, and 25 samples by varnish. The treatment agents were applied by brush until saturation of the natural stone surface was achieved. These industrial polishes were selected for their wide availability in Sanliurfa area. In order to evaluate the durability of the water-repellent treatment, the treated samples were immersed in water for 3 days. Then, the UCS (45 samples) and water absorption (30 samples) values of the polished and water-exposed samples were determined, and compared with the values of the natural and saturated samples. To further determine the best treatment alternative for SLS (i.e., the minimum water content and maximum strength), additional tests were conducted. A total of 75 samples were first dried in an oven at 105 °C for 3 days. Then, the samples were treated by three types of industrial polish (25 samples with liquid stone polish, 25 samples with polysiloxane, and 25 samples with lithium silicate), using the same approach that was used for the natural stones. After this process, the samples were immersed in water for 3 days. Then, the UCS and water absorption values of the samples were determined, and compared with the values of the natural and saturated samples. Experimental samples were taken from a commercial quarry, and prepared as cubes with dimensions of 150 ± 10 mm following ASTM C170 (1999). UCS and water absorption tests were carried out in accordance with the ASTM C170 (1999) and ASTM C97 (1996) standards, respectively.

Then, the effects of polishing on the acid abrasion of SLS were examined on 60 samples, in accordance with TS 699 (1987). These tests were conducted to assess the durability of the polished stones in relation to compounds that may be present in the environment. Sariisik and Sariisik (2011) and Sharma et al. (2007) state that the reduction in strength properties of marble was higher in an acidic environment, compared to an alkaline environment, due to the fact that a higher concentration of hydrogen ions accelerates the rate of corrosion. Since Sariisik and Sariisik (2011) determined that the most abrasive acidic solution on carbonate rocks was hydrochloric acid (HCl), HCl was used in this study. First 0.2, 0.4, 0.6, 0.8, and 1.0 % HCl acid solutions were prepared in separate basins, based on the recommendations of Sariisik et al. (2005) and TS 699 (1987). In the experimental acidic solutions, a pH gauge value was measured at a 0.0001 % sensitivity level for each solution. In Osmanbey Campus, the alkalinity of tap water was measured in the range of 130–200 mg CaCO3/L that could neutralize the related amount of HCI. Therefore, rather than tap water, distilled water (E.C: 0.055 μS/cm) was used to prepare HCl acid solutions. The experimental samples were obtained from a commercial quarry, and prepared as cubes with dimensions of 50 ± 5 mm following Sariisik et al. (2005) and TS 699 (1987). The 60 samples were dried by a convection oven at 105 °C for 3 days. The samples were divided into four sets, with each set having 15 samples. The first set was kept in natural conditions, the second set was treated with polysiloxane, the third set was treated with lithium silicate, and the fourth set was treated with varnish. The initial weight of each sample was measured before the tests. Three samples from each set were exposed to each of the five HCl acid solutions in the laboratory (Fig. 5). The effectiveness of the polishing treatment was assessed by selectively removing samples from the acid solutions over time and determining the resulting weights. Samples were removed 3, 7, 14, 21, and 28 days after exposure to the acid solutions. After removal from a given acid solution, each sample was rinsed with tap water and then dried in an oven at 105 °C for 1 day. The mass of the resulting samples was determined to the nearest 0.001 g. Surfaces of a selected set of samples were analyzed microscopically to further assess the effects of acid exposure. Color variations were also observed on the exposed samples.

Finally, brightness and discoloring of SLS after the polishing process and the potential use of SLS as marble replacement were examined. Ten natural plate SLS samples were polished with two types of industrial polishes (five samples were polished by polysiloxane and five samples by lithium silicate) using a lapping machine.

Polishing methods were selected according to the size and the shape of the test samples. After this process, the samples were evaluated visually.

## Results

### Effects of saturation, freezing-thawing, and fire on the UCS

Experiments indicated that the strength characteristics of SLS were highly affected by water content. Considering the mean values, the UCS can be reduced by up to 63 % (16.31–5.96 MPa) due to water saturation (Fig. 6a). Agan et al. (2013) also state that saturation can reduce the UCS of SLS up to 61 %. However, Turgut et al. (2008) state that saturation can reduce the UCS of SLS up to 26 %. This discrepancy may have been caused by two factors; differences in sampling location and water saturation duration. Both of these factors may have contributed to the variations in the results obtained in this study and in that by Turgut et al. (2008). As stated in Roels et al. (2000), Blows et al. (2003) and Benavente et al. (2004), quality or bed origin of the building stones could vary with location. In this study, samples were immersed in water for 7 days. Turgut et al. (2008) may have used a lower immersion duration for their tests. It must be noted that Agan et al. (2013) state that after 3 days of immersion, the unit weight of the SLS (and thus water absorption) does not change with the time increment.

Freezing-thawing reduced the UCS of SLS up to 50 % (16.31–7.88 MPa) of those under natural states (Fig. 6b). Akcansa (2012) state that freeze–thaw can reduce the UCS of SLS up to 50 %. However, Turgut et al. (2008) state that freeze–thaw cycles can reduce the UCS of SLS up to 20 %. Similar to the discussion above, this difference was likely caused by different sampling locations and different water contents of samples under natural conditions. The approximately 50 % reduction in UCS of SLS due to freeze–thaw indicates that the performance of SLS was close to concrete in this regard.

As indicated in Fig. 6c, fire can reduce the UCS of SLS up to 30 % (16.31–11.16 MPa) of those under natural states. Discoloration and reduction of strength due the fire effect is also stated by Gomez-Heras et al. (2009) for some Irish sandstones; Lam dos Santos et al. (2011) for some Portuguese limestones (nearly 50 % reduction in UCS) and granites (nearly 10 % reduction in UCS); Ozguven and Ozcelik (2013, 2014) for some Turkish limestones (nearly 30 % reduction in UCS) and marbles (nearly 15–25 % reduction in UCS); and by Brotons et al. (2013) for some

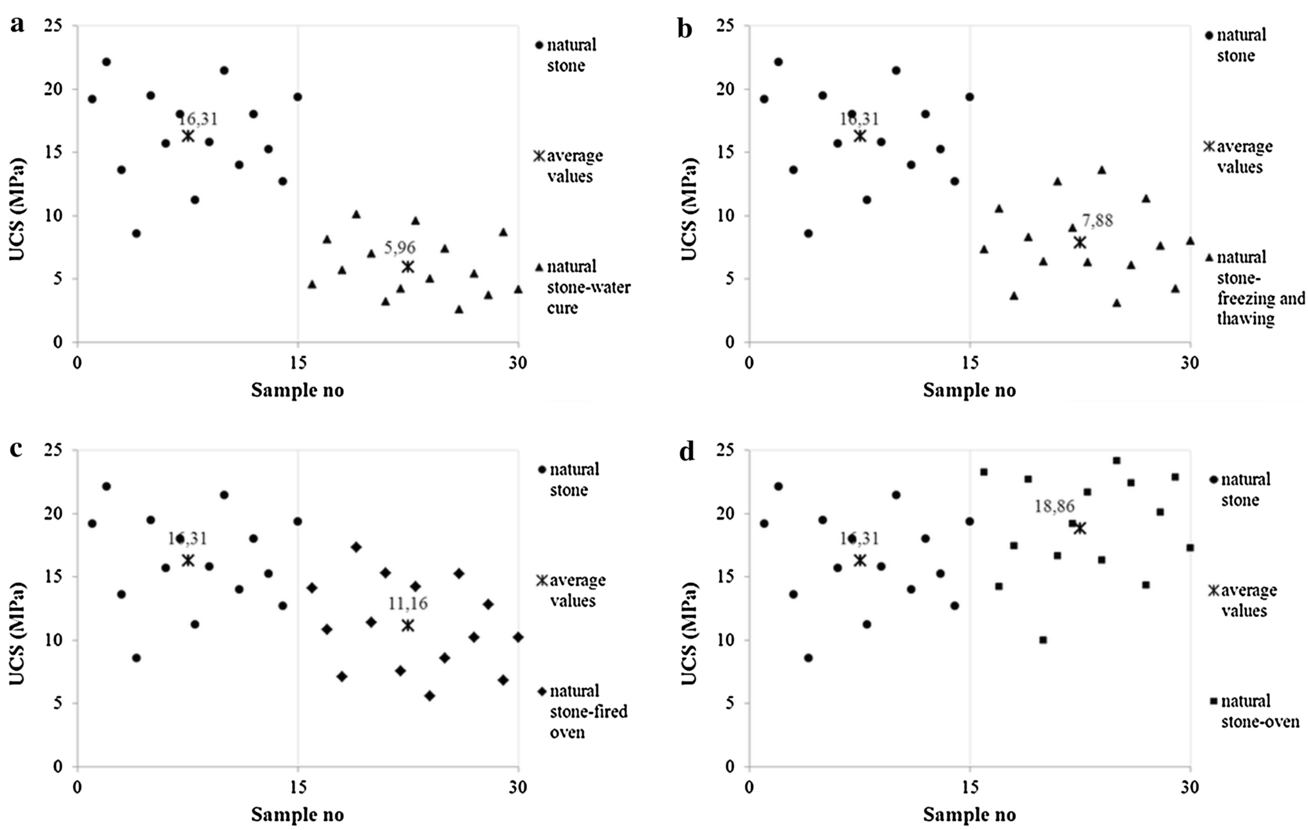


**Fig. 6** UCS test results for natural samples corresponding to (**a**) saturated, (**b**) freeze–thaw cycled, (**c**) fire exposed, and (**d**) dried conditions

Spanish calcarenites (nearly 35–50 % reduction in UCS). Neville (2000) states that concrete can lose its strength up to 50 % in a 600 °C fire. Overall, SLS has better fire resistance than concrete, some Portuguese limestones, and some Spanish calcarenites. However, some Turkish marbles, Portuguese granites, and some engineered stones are superior to SLS. It should be noted that this comparison could be misleading, because in this study, the SLS samples were exposed to fire. On the other hand, only Gomez-Heras et al. (2009) exposed their sandstone samples to fire. The other investigators mentioned above exposed their samples to heat. Likely, fire and heat might have different effects on stones. In order to obtain more definitive results, the tests should be performed under the same conditions.

Data in Fig. 6d reveal that drying can increase the UCS of SLS by up to 15 % (16.31–18.86 MPa) of those under natural states.

## Effects of polishing on the UCS and the water absorption capacity

The experiments reported above indicate that water saturation decreases the UCS of SLS. In this section, results of the performance of the polishes for preventing water absorption of SLS are presented. The results indicated that all three types of polishes (polysiloxane, lithium silicate and varnish) used in the test program were effective for maintaining the UCS of SLS by reducing water absorption. As mentioned above, water saturation can reduce the UCS of SLS by up to 63 %. By using polysiloxane, lithium silicate, and varnish, this reduction percent of UCS was decreased to 46, 41, and 38 %, respectively (Fig. 7a). By using polysiloxane, lithium silicate, and varnish, the maximum water absorption by weight percentage of SLS (12.11 %) was decreased to 11.09, 9.24, and 8.58 %, respectively (Fig. 7b). Based on these results, varnish and polysiloxane were determined to be the most and least effective polishes, respectively.

In this section, the effects of pre-drying before polishing on the UCS were examined. The testing was aimed at obtaining the maximum UCS for SLS by maximum insulation from water. As seen from Fig. 8, pre-drying before polishing increased the UCS, and decreased the water absorption potential of SLS. Based on these results, varnish and polysiloxane were also determined to be the most and least effective polishes for isolating SLS against water intrusion, respectively.

The adverse effects of water absorption level and the positive effects of polishing and pre-drying processes on the UCS of SLS are collectively shown in Fig. 9. The UCS was inversely correlated to water absorption for the samples that were tested, with the UCS decreasing with increasing water absorption. As seen in Figs. 8 and 9, the dried natural stone (natural stone-oven) samples with the minimum water absorption percent by weight provided the maximum UCS value. In contrast, the saturated natural stone (natural stone-water immersed) samples that had the maximum water absorption percent by weight provided the minimum UCS value. Figures 8 and 9 also indicate that the polishing process could increase the UCS of the SLS, because the polishes decreased the water absorption levels of the SLS samples to varying degrees. In this regard, the maximum and the minimum conservation action was provided by varnish and polysiloxane, respectively. In addition, the pre-drying process before polishing increased the UCS, and decreased the water absorption potential of SLS. The maximum UCS values (i.e., the closest to the UCS values of natural stone samples) were obtained for the pre-dried and then the treated SLS samples. As stated by Sariisik and Sariisik (2011) and Dreesen and Dusar (2004), the stones with low porosities were less affected by environmental factors. The polishes likely penetrated the dry

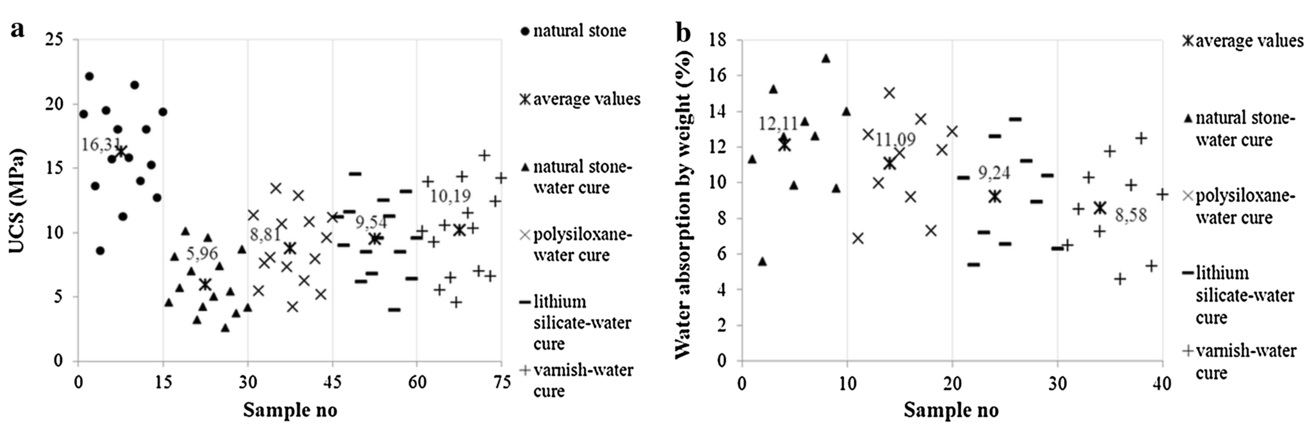


**Fig. 7** Results for (**a**) UCS and (**b**) water absorption tests on natural and treated samples

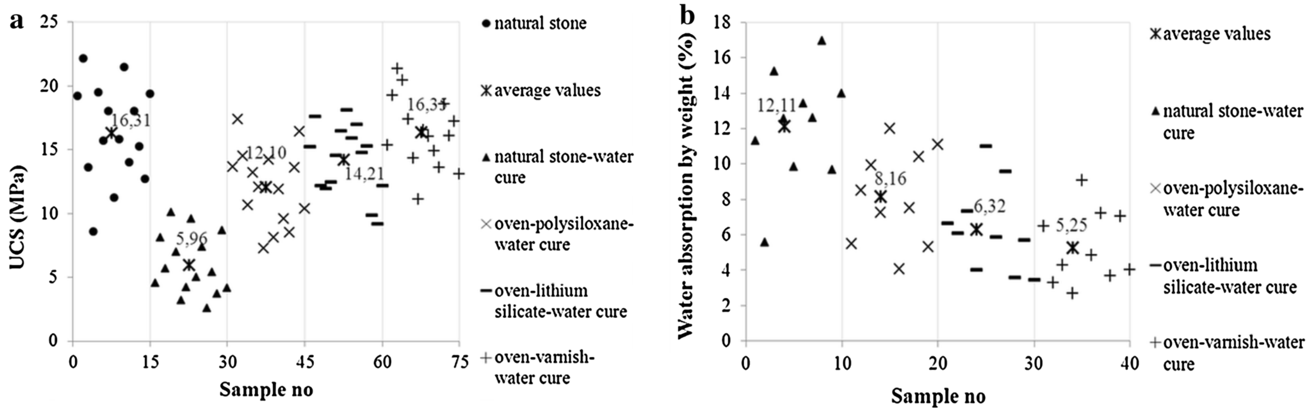


**Fig. 8** Results for (**a**) UCS and (**b**) water absorption tests on natural and dried-treated samples

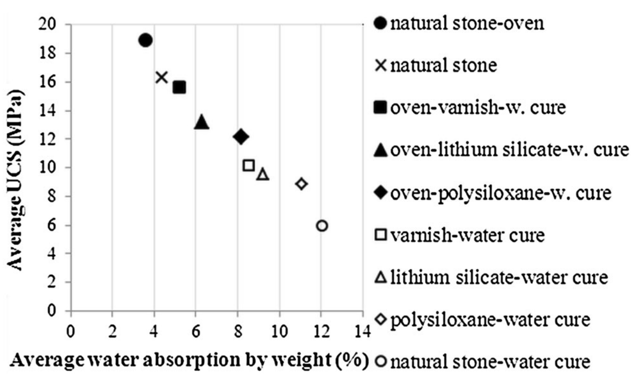


**Fig. 9** Average UCS values of the samples versus average water absorption by weight percentages

stone surface well, forming a watertight, protective film and reducing water absorption potential.

## Effects of polishing against acid attack

Some of the most damaging components of atmospheric conditions on SLS integrity consist of acid abrasion and discoloration of stones. The testing aimed at prolonging the lifetime of SLS by insulation from acid rain, and keeping the original color of the stones. The results indicate that all three types of polishes (polysiloxane, lithium silicate, and varnish) used in the test program were effective against acid abrasion. Figure 10 illustrates the average weight losses of limestone in the acid solutions with time. As seen in Fig. 10a, the average weight loss due to acid exposure increased depending on the concentration of the acid solution and duration of exposure. The maximum average weight losses were observed for the natural stones without any polish treatment. It generally took about 3 days for half of the weight loss to occur. The maximum (13 %) and the minimum (2 %) weight losses were due to exposure to 1.0 and 0.2 % HCl solutions, respectively. On the other hand, the polish treatment significantly reduced the weight loss due to acid exposure. As seen in Fig. 10b–d, by using polysiloxane, lithium silicate, and varnish, the maximum weight losses were decreased to 3.2, 0.85 and 0.52 %, respectively. Based on these results, the maximum and the minimum conservation against acid were obtained by varnish and polysiloxane, respectively. Generally, the treatments remained efficient for 14 days. However, the water-repellent treatments steadily lost their efficiency and the acid began to interact with the SLS samples after 14 days. Even though the weight losses of polish-conserved stones increased after the 14th day of testing, the total weight losses of polish-conserved stones were considered negligible compared to those under natural states (Fig. 11).

In order to demonstrate the abrasive effects of acid solutions, the unpolished natural and polished SLS samples were observed and photographed by a microscope. At first, a microscopic photograph of the initial state of the unpolished SLS was taken, as seen Fig. 12a. Then, the images of unpolished natural SLS and polished SLS samples were obtained after 28 days of acid exposure in 1.0 % HCl solution. The analysis indicated that all three types of polish (polysiloxane, lithium silicate, and varnish) were effective for the conservation of SLS against the acid abrasion effect. As seen in Fig. 12b, the maximum abrasion and pitting were observed for the natural stones without any treatment. As seen in Fig. 12c–e, by using polysiloxane, lithium silicate, and varnish, respectively, abrasions and pitting were decreased. Again, the minimum and the maximum effectiveness were observed for polysiloxane (Fig. 12c) and for varnish (Fig. 12e), respectively.

The appearances of the natural and the polished samples prior to acid exposure are presented in Fig. 13a. The first sequence is the natural samples without any conservation.

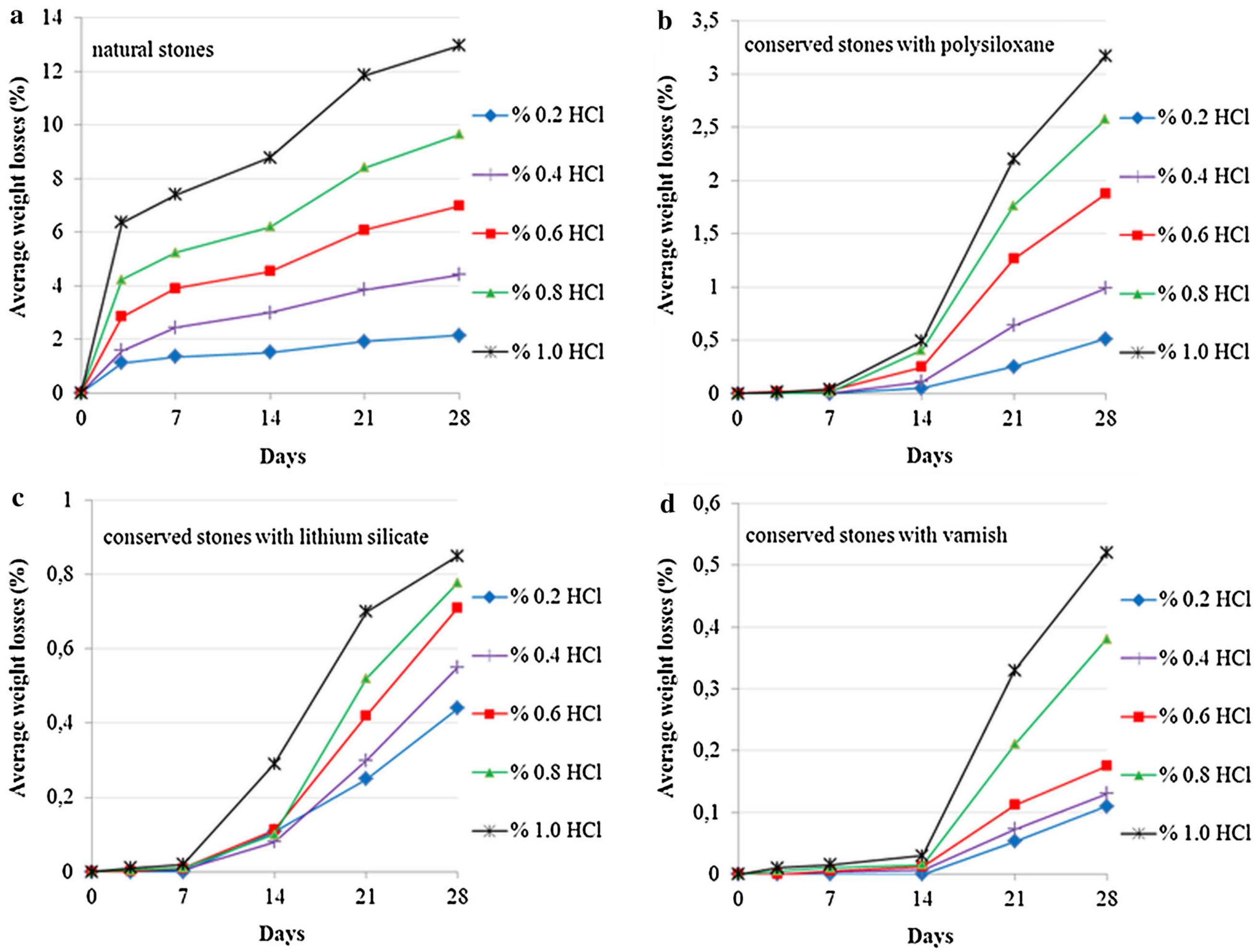


**Fig. 10** Average weight loss versus time graphs for the (**a**) natural samples, and samples treated by (**b**) polysiloxane, (**c**) lithium silicate, and (**d**) varnish

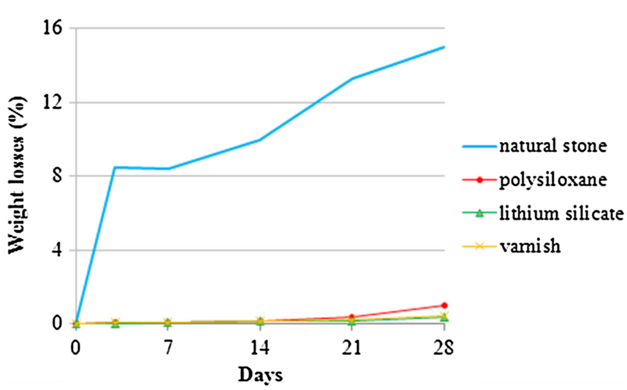


**Fig. 11** Overall graphical presentation of the average weight loss versus time

The second, third and fourth sequences are the samples that were polished by using polysiloxane, lithium silicate, and varnish, respectively. The appearances of the natural and the polished samples after 28 days of exposure to the 1.0 % HCl acid solution are presented in Fig. 13b. Although the varnish provided the maximum conservation and the roughest surface texture, this type of polish changed the appearance of the stone and caused discoloring (yellowing). Polysiloxane also changed the appearance of the stone and caused discoloring (both yellowing and darkening). In contrast, lithium silicate provided an appearance close to the original color of the stone, and the abrasion conservation degree and the roughness were close to those obtained for varnish (Fig. 12d). In this regard, the most successful abrasion resistance and color conservation was determined to be lithium silicate.

Sariisik et al. (2005) state that the upper limit of acid abrasion of marbles should not exceed 5 % of the weight of the stone. After the treatment, the maximum weight losses decreased to 3.2 %. Based on these results, it can be concluded that SLS can potentially be used as a marble stone replacement after the treatment processes.

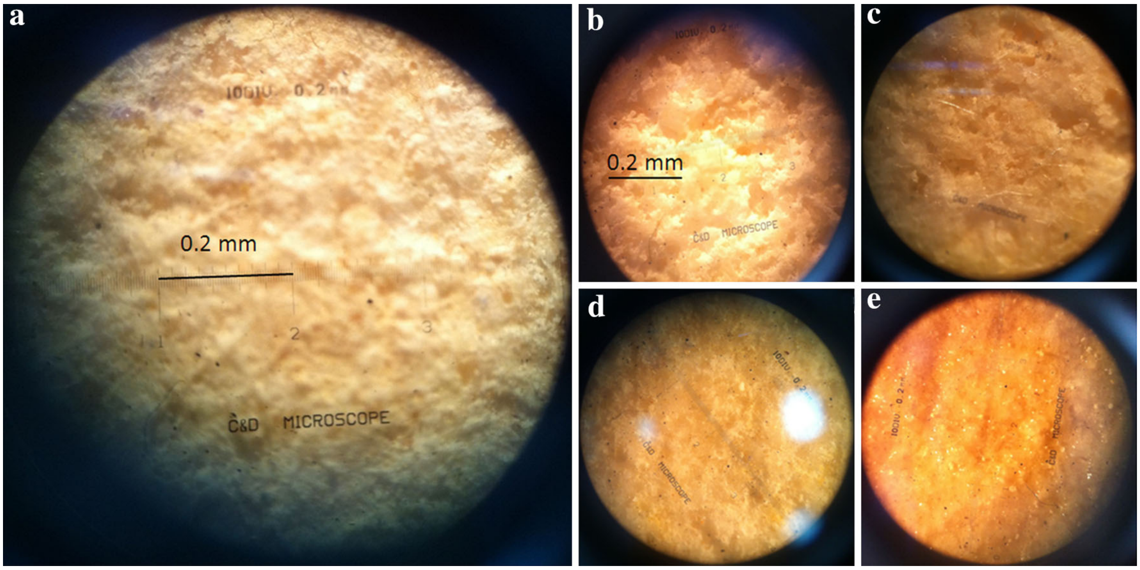


**Fig. 12** The initial microscopic view of the SLS (**a**), and after 28 days of exposure to 1.0 % HCl acid solution for the (**b**) natural sample, and the treated samples by (**c**) polysiloxane, (**d**) lithium silicate, and (**e**) varnish

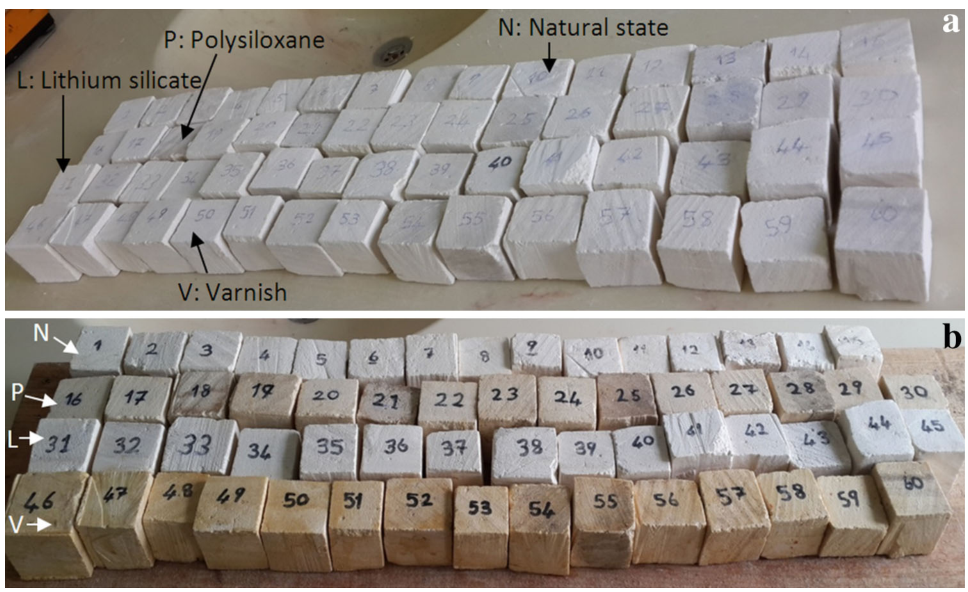


**Fig. 13** The appearances of the natural and treated samples (**a**) before and (**b**) after the acid abrasion test

### Visual performance of polishing

Within the scope of this study, the polishing performance of SLS was finally examined visually, in relation to the use of SLS as a marble substitute. The results indicate that both the lithium silicate (Fig. 14a) and polysiloxane (Fig. 14b) polishes were effective in surface treatment of the SLS plate samples. However, the best appearance and brightness were obtained from the stones that were polished by using lithium silicate. The results suggested that SLS has potential for use as a marble replacement.

## Conclusions

This study has shown that it is possible to retain the World Cultural Heritage monuments for future generations by treating them with appropriate means. Previously, there was no information on polish performance and the treatment of SLS in the literature.

The results presented herein are based on the data obtained through physico-mechanical tests, abrasion tests, polishing applications, and microscopic and visual observations.

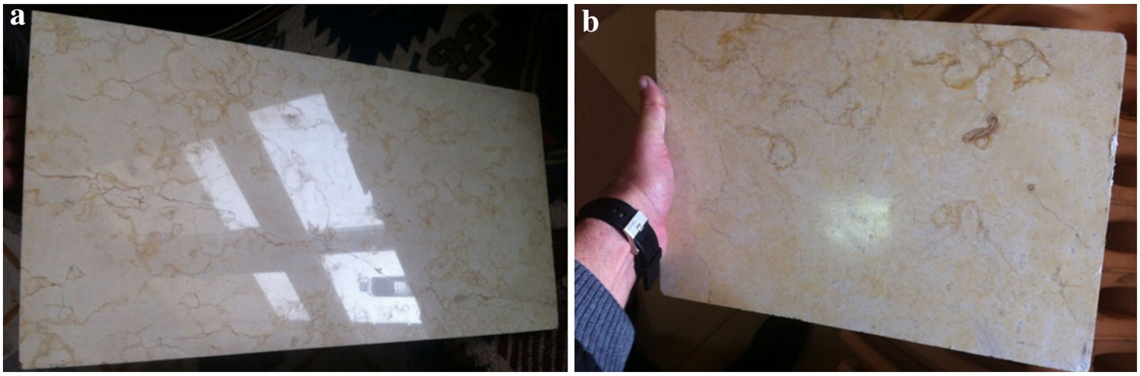


**Fig. 14** The visual performances of the polished samples (**a**) lithium silicate and (**b**) polysiloxane

Experiments indicated that compared to the natural states of SLS, the UCS was reduced due to saturation (up to 63 %), due to freeze–thaw (up to 50 %), and due to fire (up to 30 %). The SLS absorbed water up to 12.1 %. Pre-drying the SLS increased the UCS of SLS up to 15 %.

All three types of polish (polysiloxane, lithium silicate, and varnish) used in the test program were effective for conservation of SLS by reducing water absorption. Effectiveness of the polishing process for SLS was enhanced with the addition of the pre-drying step. The maximum-to-minimum water-repellent performance was obtained for varnish, lithium silicate, and polysiloxane.

All three types of polish were also effective for protecting the SLS against acid abrasion. The maximum-to-minimum acid protection performance was obtained for varnish, lithium silicate, to polysiloxane.

The microscopic and visual observations indicated that the maximum-to-minimum conservation of the SLS was obtained using varnish, lithium silicate, and polysiloxane. Based on the visual observations after the polishing processes, the performance of polishing on SLS was interpreted as satisfactory. The best brightness, appearance, and protection of the original color were observed for the lithium silicate application.

Overall, the most successful polish for the conservation of the SLS was determined to be lithium silicate. Even though the varnish provided the maximum resistance against water absorption and acid attack, the varnish changed the original appearance of the stone (caused yellowing). The polysiloxane provided satisfactory polishing and water insulation performance, yet also changed the appearance of the stone (caused yellowing and darkening).

The three most significant conclusions from the study can be summarized as:

– The strength of the SLS can be improved and polish treatment can prolong lifetime of structures that were constructed using SLS.
– The most effective polish for conserving the strength and appearance of SLS was determined to be lithium silicate.
– SLS can be successfully polished and may have a significant industrial potential as a marble substitute.

Additional testing and analysis are required in order to reach more definitive interpretations and to qualify the SLS as a marble stone. Further testing can be conducted using different types of polishes, as well as different environmental interactions (e.g., alkaline, acetic acid, and nitric acid), performance criteria, samples, and quarries with other locations that supply SLS.

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