Efficiency of protective coating applied on a highly porous decorative tuff

Tatiana Durmeková, Renáta Adamcová, Martin Maľa & Petra Grand
Comenius University in Bratislava, Faculty of Natural Sciences, Department of Engineering Geology, Hydrogeology and Applied Geophysics, Bratislava, Slovak Republic, tatiana.durmekova@uniba.sk

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Abstract: The application of protective coatings can significantly influence the essential physical properties of rocks used in building and decorative industries. This paper presents the results of laboratory tests demonstrating the positive effect of the protective coating Antipluviol S applied on a tuff from Tuscany in Italy, which is a weak volcanic rock of a very low strength and very high porosity. The efficiency of the coating was measured by absorption tests, standard uniaxial compressive strength tests and cyclic frost resistance tests. After the coating application, the water absorption decreased from 39.1% to 31.3% by total rock immersion at atmospheric pressure conditions. The water absorption only by capillary suction showed much higher efficiency of the coating. The change in the rock strength, resulting from the coating application, was less pronounced; the mean values rose from 5.8 to 6.8 MPa (17.2% increase). For all strength values are quite similar in both treated and untreated groups, as well as scattered within the groups, no relevance to the coating impact could be confirmed. But, even such a slight improvement of the monitored physical parameters has the effect of slowing down the rock's weathering. This was proven by the results of the frost resistance test. Coated samples withstood all the standard 25 freeze-thaw cycles, whereas untreated samples began to disintegrate after the 17th test cycle. These findings can help the maintenance of the famous historic architecture of picturesque tuff towns of Tuscany suffering from weathering, and contribute to the preservation of the cultural heritage. On the other hand, they showed how important such tests are when considering building stone import.

Key words: Tuscany tuff, weathering, protective coating, water absorption, UCS, frost resistance

1. INTRODUCTION

Each type of natural stone has an encoded specific disposition for certain behaviour under the impact of weathering agents. The genesis, mineral composition, and structural-textural features of the rock are essential internal factors affecting the stability, durability, weathering resistance, and thus the rock material's longevity. To increase the durability, the application of protective coatings on natural stones exposed to external conditions in building facades, decoration etc. became the current standard technique. The coating serves as a suitable prevention from weathering. Practitioners in the restoration of historical sites, mainly statues and valued architectonical elements made of stone, are probably the most experienced in applying protective mediums (Beck et al., 2003; Doehne & Price, 2010). The domestic and international market offers various impregnation coatings and promotes new products being under development. The recently developed products against the negative impacts of external conditions are based on chemical nanotechnology, which means that the main particles are in nanometers. Their effect is tested and described mainly on high-quality natural stones used on historical buildings, e.g. marbles (Aldoasri et al., 2017; Ban et al., 2019). The interactions between chemical products and the natural stone, as well as the impact of protective coatings on the stone material are continuously tested and analysed in chemical laboratories (Wheeler, 2005; Török et al., 2006; Pedna et al., 2016). The producers evaluate the water resistance of the coating and the general impact of the formed protective layer that should repel water, make the material maintenance easier, and prolong its durability. The available literature sources do not provide sufficient research data on the durability of protective coatings on natural stones or equivalent stone products. Questions as how long does the protective effect last, or how often the coating has to be applied on the stone surface, are still unanswered. The problem of a different impact when the coated stone is exposed to permanent water contact or just to sporadic rain, is also not resolved. Only the time, i.e. a long-lasting exposure, can truly verify the effect of the applied coating. However, some indication and material behaviour models can be determined by accelerated weathering tests in the laboratory.

As good as no relevant data are available about protective coatings on highly porous stones, e. g. tuffs. Their particular structure, built by primary pores of the size of macro-pores (i.e. pores visible by eye) and hollows between mineral grains, predetermine the rock to be an excellent material for decorative use. Typical properties of the tuff (i.e. light, highly abrasive, easy to carve and shape) make it a suitable stone for face ashlars, sculptural arts, or for production of small architectural elements. Tuffs are widely used as building stone in Central Italy (Colella et al., 2017; Heap et al., 2018). But, this is a rock of lower strength that is prone to decay in a relatively short time. The picturesque medieval stone towns and villages like famous Pitigliano (Fig. 1), attracting numbers of tourists and visitors, suffer under intense weathering. Both the preservation and remediation of these historical and cultural jewels require scientific approaches.

In 2008 an international symposium "Conservation and Sustainable Development of the Tuff Towns", convened by the World Monument Funds, took place in Pitigliano, Civita di Bagnoregio and Orvieto (Barbacci & Peruzzetto, 2010). The focus of the symposium was to address geological and cultural sustainability

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Fig. 1: **Panorama of the tuff town Pitigliano in Tuscany, Italy (Stendardo P. S., https://pixabay.com, free download and use, 2021-03-21).**

issues. Papers in the symposium proceedings clearly state that weathering of the high tuff cliffs and the plastic deformation of thick layers of clays in the subsoil are the reason of their geological instability, leading to landslides and rock falls (Baffo, 2010; Canuti & Fanti, 2010; Delmonaco et al., 2010). Many historic hill towns of Tuscany, Umbria, and Lazio exist in a distinctive geological landscape carved out over millions of years from a volcanic tuff plateau. The shared geology of these regions means that the tuff towns face similar problems of erosion and potential collapse of the cliffs that support them. These threats to their built heritage are increasing with time. The problem of cultural heritage conservation in geomorphologically hazardous areas, like the tuff towns of the Tuscany historical region, is generally ruled by two different approaches: i) an engineering-geology-driven approach that exclusively takes into account stabilization and reinforcement of the physical landscape and structure; ii) a cultural-heritage-driven approach, mainly focused on the preservation and conservation of the built heritage, where the main concerns and expertise are in archaeology, architecture or art conservation. Usually one approach is used without regard to the other, so that some aspects of the problem are underestimated or not even considered (Delmonaco et al., 2010). While different interventions and remediation actions regarding cliffs´ stability were presented, less attention was paid to the decay of the tuff architecture. Bianchini (2010) pointed at the sense of decay that is apparent in various parts of the towns, and which makes them appear worse than the actual condition warrants (Fig. 2). She underlined that no major achievement, regardless of its importance and level of complexity, will ever express its full potential unless attention is paid to the details, the finishes, however marginal or small they may seem. Small things help achieve "great things". As a contribution to such conservation and remediation effort, the efficiency of a commercial protective coating applied on the surface of similar tuff from the central Italy was evaluated using absorption and frost resistance tests; the last ones simulate accelerated weathering tests. The results are presented in this paper.

2. MATERIALS

The examined tuff rock comes from the southern part of Tuscany region in Italy, province of Grosseto, near the Pitigliano village. The territory of southern Tuscany, on the border with Lazio region, is characterized by the presence of extensive pyroclastic deposits linked to the activity of the Latera volcano (part of the western Vulsini Volcanic District), the activity of which developed between 280 and 160 Ma ago (Pecerillo, 2010; Fratini & Rescic, 2013). The tuff is a product of the Pleistocene magmatic activity (Marroni et al., 2015). The tested tuff is a relatively fine-grained volcaniclastic rock, lithic fragments and mineral grains larger than 2 mm were rare. The rock colour is pleasantly warm, seemingly light brownish yellow, but identified as pale brown (symbol 2.5Y 8/2) according to Munsell Color Charts (2010). As the mineral composition was not known, mineral analysis was included into the research.

One commercial supplier intended to bring this natural stone to the building material market in Slovakia. He offered and delivered the tuff for the laboratory research in the form of rock monoliths measuring approximately 30 cm x 20 cm x 20 cm. Test samples were produced from monoliths by cutting, using parallel saws. More than 70 test samples in the shape of cubes with the edge length of approximately 50 mm were prepared (Fig. 3).

Fig. 2: Selective weathering of the tuff facades is less evident from the distance; a walk in the historic center of Pitigliano reveals the building stone decay (Mantu A., https://pixabay.com, free download and use, 2021-03-21).

For the coating, the commercial product Antipluviol S from the Italian producer MAPEI was selected. This is intended to protect stone and similar building materials against adverse weather conditions. It is based on siloxane resins. It is a colourless transparent liquid specified by the producer as a water repellent suitable for impregnating walls, non-glazed ceramic tiles, concrete and all absorbent mineral products (stones) used in building, primarily aimed as protection against rain. It is applied to the material's porous surface, penetrates deeply and reacts with aerial humidity and natural moisture in the material, thus forming a water-repellent layer inside pores and capillaries. Antipluviol S does not form a separate layer or skin on the stone surface and,

Fig. 3: Tuff samples. a – one part of the tuff cubes prepared for the application of the protective coating; b – a more detailed view of the tuff showing the remarkable macro-porosity.

therefore, it does not significantly modify permeability to water vapour. The producer also states that this product is classified as dangerous, highly flammable and harmful for the environment.

3. METHODS

Chemical analysis of the untreated rock material was performed by the Electron Probe Microanalyzer (EPMA, electron microprobe), and the mineral content of the lithotype was identified. For this purpose, polished thin sections coated with a thin film of conductive material were made of the natural stone.

Basic physical properties of the tuff in its intact natural state were determined, namely bulk density ρ_d (kg.m^{-3}), particle density ρ_s (kg.m^{-3}), total porosity *n* (%), open porosity n_o (%), water absorption at atmospheric pressure by complete immersion *WAI* (%), the water absorption by capillarity *WAC* (in % or g.m^{-2}) and uniaxial compressive strength *UCS* (MPa). For the tests of *WAC* (also called sorptivity), samples were immersed in water to a height of 3 ± 1 mm in a plastic tank on non-absorbent and non-oxidizing pads. Water was sucked into the unsaturated part of the sample by the capillary rise. The time intervals used for measuring the mass increase due to absorbed water was given: 1, 3, 5, 10, 15, 30, 60, 120, 180, 240, 360, 480 and 1440 minutes. *WAC* was evaluated from the mass of the water absorbed at a specified time. The final capillary water absorption coefficient C_f (g.m^{-2}.s$^{-0.5}$) was calculated from the absorption curves at the time *t* = 1440 min, as follows:

$$C_f = \frac{m_t - m_d}{A.\sqrt{t}} \qquad (1)$$

where m_t (g) is the mass of the sample determined at the time *t* (s) since the first contact with water, m_d (g) is mass of the dried sample, *A* (m^2) is the area of the sample base in contact with water.

C_f is a key parameter characterizing the water absorption capability of porous building materials, which is essential to the simulations of moisture transfer (Lu et al., 2020). It can be calculated in the cases when capillary curves in their first part are linear.

These properties were determined according to valid technical standards. Densities and porosities were determined according to EN 1936: 2007, *WAI* according to EN 13755: 2008, *WAC* test was carried out according to EN 1925: 1999 and *UCS* test according to EN 1926: 2007. The apparent (envelope) volume of samples required in order to calculate ρ_d was determined by hydrostatic weighing of water-saturated samples. For this purpose, as well as to determine the water absorption, the samples were saturated with water until reaching a constant mass of the samples. Particle density ρ_s was determined by the pycnometric method applying the rock pulverized to a fine powder. Where appropriate to dry the samples, these were always dried to a constant mass in the ventilated oven at a temperature of 70 (± 5) °C. The average values of ρ_d and ρ_s were used for the calculation of the total porosity *n* (%) as follows:

$$n = \left(1 - \frac{\rho_d}{\rho_s}\right) \cdot 100 \qquad (2)$$

The open porosity n_o (%), which is defined as the ratio of the volume of pores accessible by water to the total volume of the sample, was similarly determined by calculation according to the formulas given in the standard EN 1936: 2007:

$$n_o = \frac{m_{sat} - m_d}{m_{sat} - m_h} \cdot 100 \qquad (3)$$

where m_d (g) is mass of the dried sample, m_{sat} (g) is mass of the saturated sample and m_h (g) is mass of the saturated sample weighted in the water.

The open porosity n_o depends on the diameter of the pores where water molecules can get in or pass through, so it is always lower than the total porosity *n*: some pores are too small for water, but they contribute to *n*. The above mentioned *WAC* reflects primarily the transport mechanism for water in the tiny open connective pores in materials due to surface interaction forces between the water and the pore wall (Singh, 2018), acting even against the gravity. For capillary rise decreases with increasing capillary diameter, large macropores remain empty in the upper part of the sample that was not immersed in water. This is the main difference to the WAI test, where the sample is exposed to both, the hydrostatic pressure and the capillary forces, and big open pores are easily filled with water during saturation from all sides.

One portion of the prepared tuff cubes was treated with a protective coating Antipluviol S: 3 samples for the *WAC* test, 6 samples for *WAI* and the following frost resistance tests. The coating was applied twice, to the entire surface of the test cubes, with a flat brush, according to the producer's recommendation, at least two hours apart (Fig. 4).

To verify the coating's efficiency, the coated samples underwent the standard laboratory tests of WAI and WAC, and results were compared with the same number of untreated samples.

The frost resistance test is relatively simple and very efficient, but quite time demanding. 12 cubes were selected and divided into two groups of 6 cubes. One group consisted of samples in their natural state, the other group of samples was treated with a protective coating of Antipluviol S. The coating was applied to all surface areas of the cubes. Prior to the frost resistance test, the samples were dried to a constant weight, and their mass was determined. Subsequently, the samples were allowed to saturate with water in a water bath for (48 ± 2) hours, after which time they were removed from the water bath, surface-dried with a damp cloth, and the mass of the saturated samples was determined. In this manner, the samples were prepared for the freezing. The frost resistance test consisted of cyclic freezing and thawing of all 12 test specimens. Each test cycle consisted of a minimum of 4 hours of freezing at a temperature below –12 °C and a minimum of 2 hours of thawing with the samples completely immersed in water at (20 ± 10) °C. It was planned to perform 25 freezing cycles according to STN 72 1800:1987. In the case of the sample disintegration before reaching the final number of cycles, the number of cycles that the samples have withstood without loss of cohesion is indicated. The assessment of the frost resistance involves the comparison of the samples´ weight before and after the test, as well as of *UCS* of the rock before (symbol UCS_o) and after 25 freeze/thaw cycles (symbol UCS_f), in accordance with

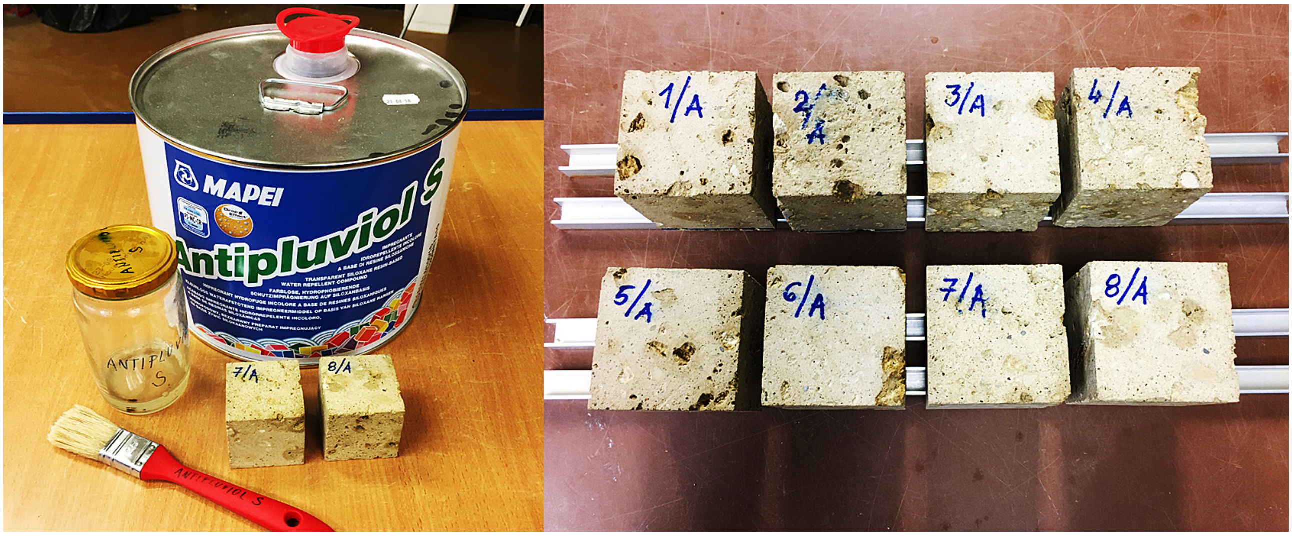

Fig. 4: Tuff samples impregnated by the protective coating Antipluviol S.

the implementation of the so-called technological test (EN 12371:2010). It is also possible to determine the frost resistance coefficient K_{FR} (dimensionless), which is stated as one of several technical parameters specifying the use of rocks for dimension stone products (STN 72 1800: 1987). The coefficient expresses the change in strength of the rock after the frost resistance test and is calculated for *UCS* as follows:

$$K_{FR} = \frac{UCS_f}{UCS_o} \quad (4)$$

4. RESULTS

The mineral composition of the tuff proved to be very varied. Except for the volcanic glass, which forms the rock matrix, minerals as quartz, potassium feldspar, plagioclase, biotite, calcite, apatite, albite, clinopyroxene, titanite, titaniferous magnetite, spessartine were identified (Fig. 5). Rock fragments and rests of the juvenile organic phase are also present. Different sizes of mineral grains and lithic clasts, as well as the presence of macropores, cause the structural and textural heterogeneity of the tuff material.

The basic physical properties of the untreated tuff are given in Tab. 1. The tested material is very light, highly porous. This tuff can be classified as a soft and weak rock (STN 72 1001: 2010), because its *UCS* is low, but it is still stable in contact with water.

Tab. 1: Physical properties of the untreated tuff

Property/characteristic	Mean value
Bulk density ρ_d (kg.m^{-3})	1 046
Particle density ρ_s (kg.m^{-3})	2 288
Total porosity *n* (%)	54.3
Open porosity n_o (%)	40.2
Water absorption *WAI* (%)	39.1
Uniaxial compressive strength *UCS* (MPa)	5.8

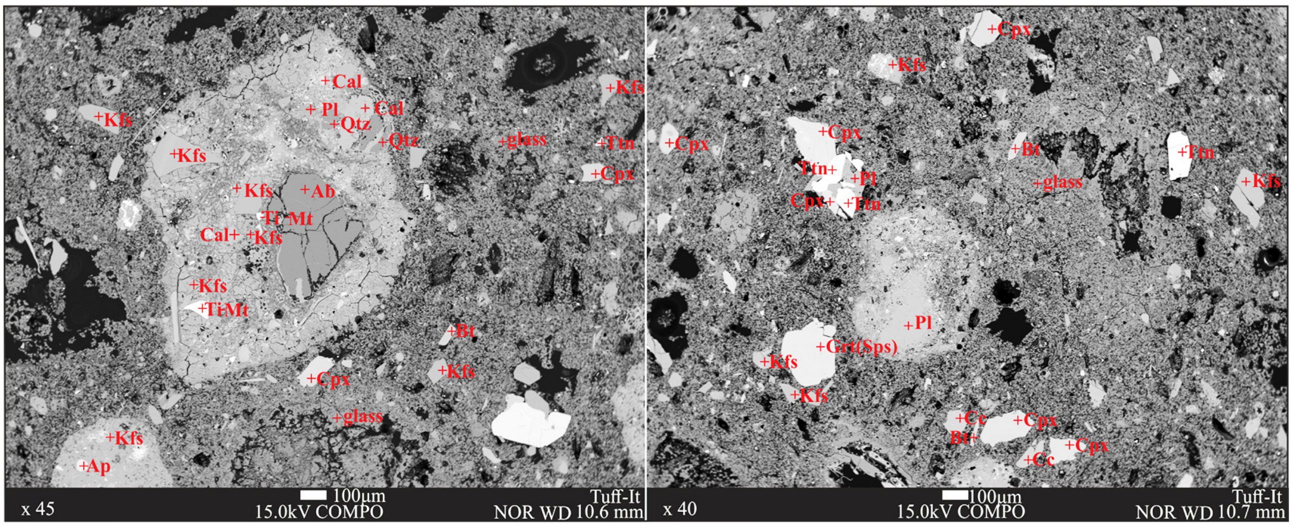

Fig. 5: Minerals identified by EPMA microphotos in the untreated tuff. Kfs – potassium feldspar, Pl – plagioclase, Qtz – quartz, Cal – calcite, Ttn – titanite, Cpx – clinopyroxene, Ap – apatite, Ab – albite, Bt – biotite, Ti-Mt – titaniferous magnetite, Grt(Sps) – spessartine garnet.

The effect of the protective coating upon the tuff´s properties is evident from Tab. 2, in which the most significant technical parameters are compared. All of them improved after the use of the transparent (invisible) coating. The coated samples are slightly darker, but the colour change is not very significant – from 2.5Y 8/2 to 2.5Y 7/4, which is still classified as pale brown (Munsell Color Charts, 2010). Decreased values of the both types of water absorption confirmed the hydrophobic effect of the coating.

Tab. 2: Compared physical properties of the tuff before and after the application of the coating Antipluviol S – mean values from 6 samples in each group

Parameter	Untreated samples	Samples with protective coating
WAC (%)	31.5	1.5
WAC (g.m^{-2})	16 391	771
WAI (%)	39.1	31.3
UCS (MPa)	5.8	6.8
	min/max: 3.8 / 7.8	min/max: 6.1 / 7.4

WAC testing has proven to be a very suitable method for the evaluation of the efficiency of the protective coating of the natural stone. This statement can be documented by the mean values of *WAC* and by the diametrically different time-related absorption curves of the untreated and treated tuff samples (Fig. 6). Significant differences are visible between the values of the absorption coefficient C_f (Fig. 7, Tab. 3) that were calculated from the absorption curves. Performed tests have shown that the protective coating Antipluviol S had a significant effect on *WAC*.

Photographs in Fig. 8 document the very high capillary water absorption potential of studied tuffs in their untreated natural state and the efficiency of the used protective coating. The difference in the visual appearance of the samples treated and untreated with Antipluviol S and immersed in water is evident from Fig. 9. While the untreated sample looks dark and fully saturated at the end of the test, the appearance of the coated samples with Antipluviol S remains unchanged, seemingly dry.

Tab. 3: Results of the capillary water absorption coefficient C_f after 1440 min

	Untreated natural samples			Samples with protective coating		
	1N	**2N**	**3N**	**1A**	**2A**	**3A**
C_f (g.m^{-2}.s$^{-0.5}$)	55.108	53.520	49.410	1.956	1.890	1.756
Mean		**52.679**			**1.867**	

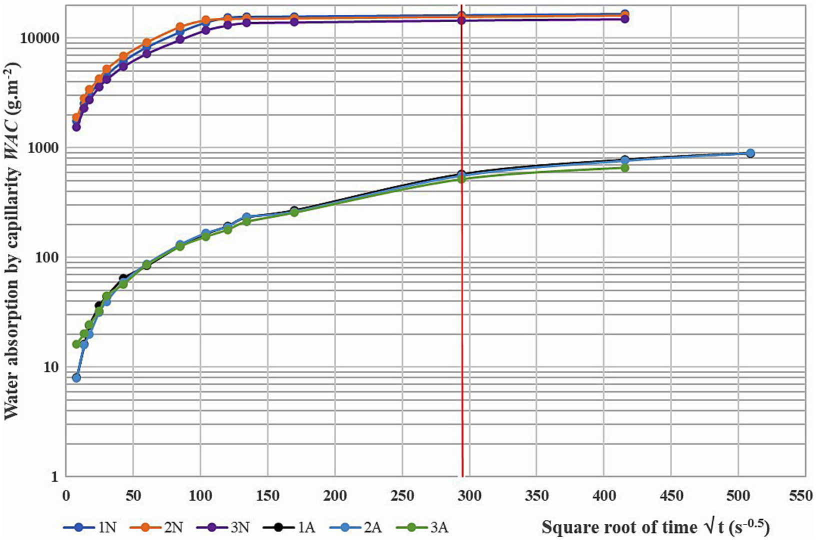

Fig. 6: Representative water absorption curves by capillarity. N – natural samples, A – samples coated with Antipluviol S, red line – t = 1440 min.

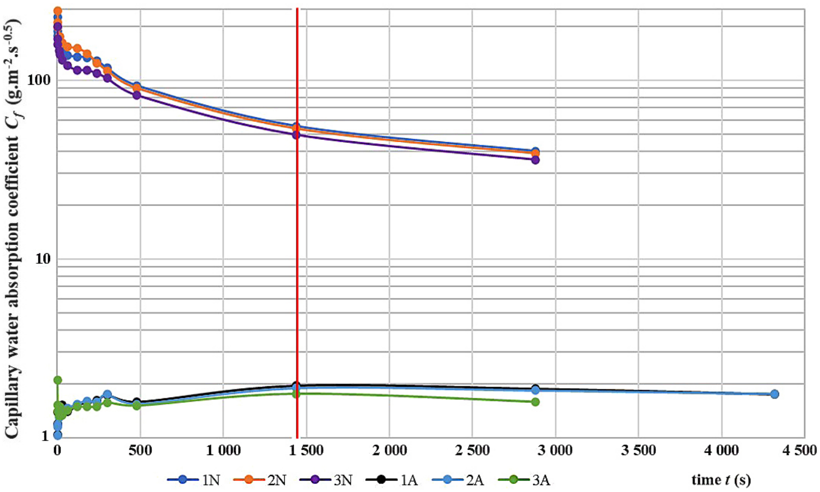

Fig. 7: Capillary water absorption coefficient in time relation. N – natural samples, A – samples coated with Antipluviol S, red line – t = 1440 min.

The results of the frost resistance test are presented in Tab. 4 and Tab. 5. In Tab. 4, the change in the weight of the samples due to cyclic freezing and thawing is evaluated. The samples' weight after the frost resistance test is expressed for those samples, which have sustained 25 cycles without failure. In the event of samples disintegration, the number of freezing and thawing cycles that the samples withstood intact is expressed. In Tab. 5, the changes in the UCS values are presented.

5. DISCUSSION

The open porosity plays an important role in the rock weathering (Adamcová, 2012; Adamcová et al., 2014). When porous materials are put in contact with water, water will be absorbed by capillary rise depending on the open pore diameters. The process of water penetration into porous building materials and knowledge of the water movement is very important for their durability and degradation mechanism assessment, authors dealing with porous natural materials in construction agree on this (Ružička et al., 2012; Ružička & Durmeková, 2012; Sengün et al., 2015; Lubelli et al., 2017). Besides the well-known degradation

Fig. 8: **Progress of the water absorption by capillarity over time is evident from the colour change of the saturated part in the yellowish tuff samples (compared to a grey low-porosity andesite as a contrast). a – after 10 minutes, b – after 30 minutes, c – after 60 minutes, d – after 2 hours, e – after 3 hours, f – after 4 hours. Explanatory notes: the first cube from left to right is an untreated sample in all photos; the second one is the sample coated by Antipluviol S.**

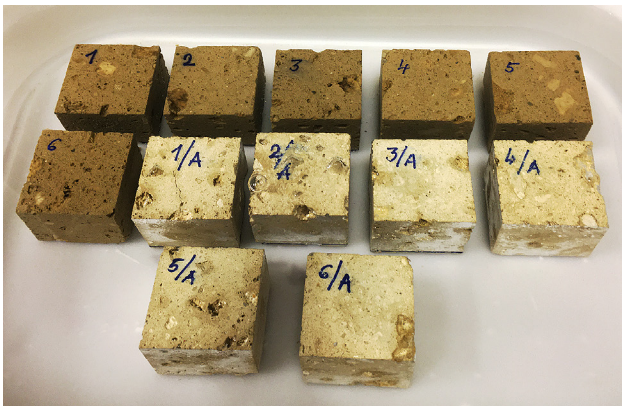

Fig. 9: **Macroscopically visible differences between the untreated specimens (No. from 1 to 6) and impregnated ones (No. from 1/A to 6/A) immersed in water.**

effects due to the volume increase at the phase transition from liquid water to solid ice during freezing, aggressive ions such as chlorides or sulphates in pore solutions can be transported deep into the material (Zhang et al., 2011). The total porosity *n* of the investigated tuff is more than 50 vol. %, whereas almost 80 % of the pores are open and accessible by water for the mentioned deteriorating processes; this looks to be critical.

However, chemically based preservative products are readily available on the market and new ones are still being developed. So, why not to use them to improve the tuff building stone quality or to preserve of the built cultural heritage? In the famous Italian Tuscany region, many houses or whole villages were constructed using local tuff in the past. Tuff as the foundation subsoil and also as the building stone. A very macro-porous weak volcanic rock prone to accelerated alteration. While stability problems of the weathering tuff cliffs under several tuff towns are by far more dangerous and more difficult to solve (Baffo, 2010; Canuti & Fanti, 2010; Delmonaco et al., 2010), the weathering of the building tuff facades should not be trivialized (Bianchini, 2010). Because tuff is a very heterogeneous material, selective weathering occurs quite often on the houses. Building stones, that remained in satisfying state for ages in the walls, join visibly decayed stones, selectively weathered and disintegrated at weaker parts (Fig. 2). Once preferred, today the same building stone would not meet the much higher quality criteria than in the past to prevent such decay.

The Slovak Technical Standard STN 72 1800: 1987 specifies the technical requirements for natural stone intended for commercial stone products with following limits: the minimum ρ_d is 1 800 kg.m^{-3}, and 15 MPa is the minimum *UCS*, the maximum *WAI* is 15% and K_{FR} must be higher than 0.75. The frost resistance coefficient K_{FR} of the tuff treated by coating was calculated 0.78. This value is very close to the limiting value of 0.75 which is the minimum given in this standard. In the group

Tab. 4: Impact of the frost resistance test upon the mass of the samples

No.	Mass of dry tuff before test m_o(g)	Mass of saturated tuff before test m_{sat} (g)	Mass of dry tuff after 25 freezing-and-thawing cycles m_f (g) or number of completed cycles (in the case of disintegration)	Loss of mass $m_o - m_f$ (g)
		Untreated samples:		
1.	117.00	170.62	17 cycles	n. a.
2.	120.27	168.71	17 cycles	n. a.
3.	132.23	179.84	17 cycles	n. a.
4.	127.19	176.00	126.19	1.00
5.	131.24	177.84	126.46	5.49
6.	131.95	178.67	20 cycles	n. a.
		Samples impregnated by Antipluviol S:		
7.	131.98	168.64	130.63	1.35
8.	128.65	155.74	127.26	1.39
9.	132.46	162.72	131.29	1.17
10.	132.29	169.95	130.98	1.31
11.	125.08	163.94	123.89	1.19
12.	130.27	164.62	129.19	1.08

n. a. = not applicable, sample disintegrated during the test

Tab. 5: Impact of the frost resistance test upon *UCS* of the samples

No.	Sample dimensions (mm) edge a	Sample dimensions (mm) edge b	Max. loading force *F* (kN)	*UCS* after 25 cycles of the freezing and thawing (MPa)
Untreated samples:				
1.				n. a.
2.				n. a.
3.				n. a.
4.	49.96	49.85	11.4	4.6
5.	49.57	49.94	13.0	5.3
6.				n. a.
UCS mean value: 4.9 MPa				
Samples impregnated by Antipluviol S:				
7.	49.67	49.70	10.6	4.3
8.	49.91	49.51	11.1	4.5
9.	49.73	49.69	13.6	5.5
10.	49.74	50.00	15.8	6.4
11.	49.84	50.34	12.7	5.1
12.	49.60	49.51	14.5	5.9
UCS mean value: 5.3 MPa				

n. a. = not applicable, sample disintegrated during the frost test

of samples not treated with protective coating, this parameter is not justified to determine due to the disintegration of up to 4 samples from the 6 examined ones. Besides K_{FR}, all other criteria preclude the use of examined Tuscany tuff in construction for recent commercial purposes – it is not acceptable with or without coating. Only less demanding users can be satisfied with such a natural material, which is suitable only for short-term purposes like fencing, fireplaces, graves, monuments, garden architecture.

Ban et al. (2019) state that all impregnation products they studied induced a clear increase in the dynamic modulus of elasticity and *UCS* of studied porous limestones and sandstones. Similar experience is presented by other authors, too. In comparison with the fresh limestone, Sahlin et al. (2000) declare increasing bending strength of the impregnated limestone, which is often a more important property of decorative rocks than *UCS*. The application of the preservative coating Antipluviol S has really slightly increased the mean value of *UCS* of the tested tuff rock (Tab. 2 and Tab. 5). But, the natural rock heterogeneity is too big, the number of tested samples too small, the results of *UCS* quite scattered and their differences with and without impregnation are negligible. Therefore, any increase in cohesive forces between the rock particles could not be confirmed after the application of the coating.

But, the impregnation with Antipluviol S can help to slow down the combined physical and chemical weathering impact of the capillary water in the building rock of the historic structures and to preserve the architectural heritage. The color change after the application is as good as invisible and it does not change even in contact in water. On the other hand, wet untreated tuff can be recognized from distance. The impregnation makes the pore walls water-repellent and changes the capillary forces. It is best visible on the results of *WAC*. The untreated tuff is saturated very fast, quickly reaching the constant value that is very high; the absorption in the impregnated tuff is more than 10-times lower, however, it still did not reach the maximum, the absorption curves are permanently increasing, also when one sample was tested for 72 hours (Fig. 6). It would be interesting to continue to see, what would be the maximum absorption capacity of the impregnated sample, and how long would it last to reach that maximum. The difference between the treated and untreated samples is very well pronounced in Fig. 7, as well. Except the scattered start, the time-related results of C_f are very consistent for all three samples in every sample group. Therefore, the test on the water absorption coefficient by capillarity C_f becomes popular in natural stone evaluation (Sariisik et al., 2010; Tomašić et al., 2011; Dinçer & Bostanci, 2019). It is highly recommended to use it in the practice to a greater extent.

The total immersion in water may damage the stone impregnation. It was manifested by this kind of the water absorption tests; all results of *WAI* were quite similar regardless of the sample preventive treatment. Based on this experience, the coating Antipluviol S was recommended to protects the Tuscany tuff and alike building stones explicitly from air humidity, occasional rain, and to mitigate the water penetration by capillary rise from the surrounding environment. These are exactly the situations present at the historical architecture of tuff towns in Tuscany, a long-time contact with water is not expected. Furthermore, such severe frost conditions as in the frost resistance tests are not usual in that region. The climate is generally mild, the winter temperatures seldom drop below 0 °C (occasionally to -7 °C in Florence; https://en.wikipedia.org), with relatively little rainfall, and the rock is not fully saturated with water. This leads to the conclusion, that the weathering resistance of the tuff impregnated with the tested preventing coating Antipluviol S will be even better in Tuscany than manifested in the laboratory.

6. CONCLUSIONS

It is certainly safer and environmentally friendly to use building stone in its natural state without any protective chemicals. Unfortunately, the given genetic predispositions and the unavoidable ageing of natural materials, especially in undesirably changing environmental conditions accelerating the decay processes, is not in compliance with today's growing demand for durability and maintenance-free needs. The paper presents particular research results referring to the efficiency of the application of a chemical coating product on the tuff rock from the Tuscany territory, famous for its tuff towns like Pitigliano and others. They are suffering from weathering, and preservation of their tuff buildings is desired. To make the application cost-effective for the practice, the Italian, i.e. local coating product Antipluviol S was selected for the investigation. Water absorption tests and frost resistance tests by repeated freezing-and-thawing cycles were used to simulate accelerated weathering conditions. They showed that all of the tuff's examined properties improved to certain degree after applying the Antipluviol S coating. This indicates a promising prolongation of both durability and usability of this tuff after such treatment. The water absorption by capillarity showed the most striking difference between the untreated samples and the coated ones. The remarkable improvement is due to the water-repellent effect of the impregnation, pointing to Antipluviol S as a suitable, stabilizing and protective coating also for this macro-porous weak rock in historic facades, being not in contact with water for longer time. But, the total immersion in water may damage the stone impregnation.

The situation would change, if the same tuff should be considered as building stone in Slovakia with its frosty winters and heavy rains. With or without preventive coating, such material is forbidden as construction material for commercial purposes due to its low *UCS* and low frost resistance (STN 72 1800: 1987). The provenance must be considered when importing any stone from countries with very different climate. Tuff used in Tuscany architecture for ages would weather and disintegrate much faster in Slovakia. Therefore, just the water-repellent effect of the protective coating without considerable improvement of *UCS* will not help. This is not a good news for the potential importer. However, this stone is suitable for interior decorations because of its attractive appearance, or, with the preventive coating application, for less demanding exterior elements like fencing, garden architecture etc.

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