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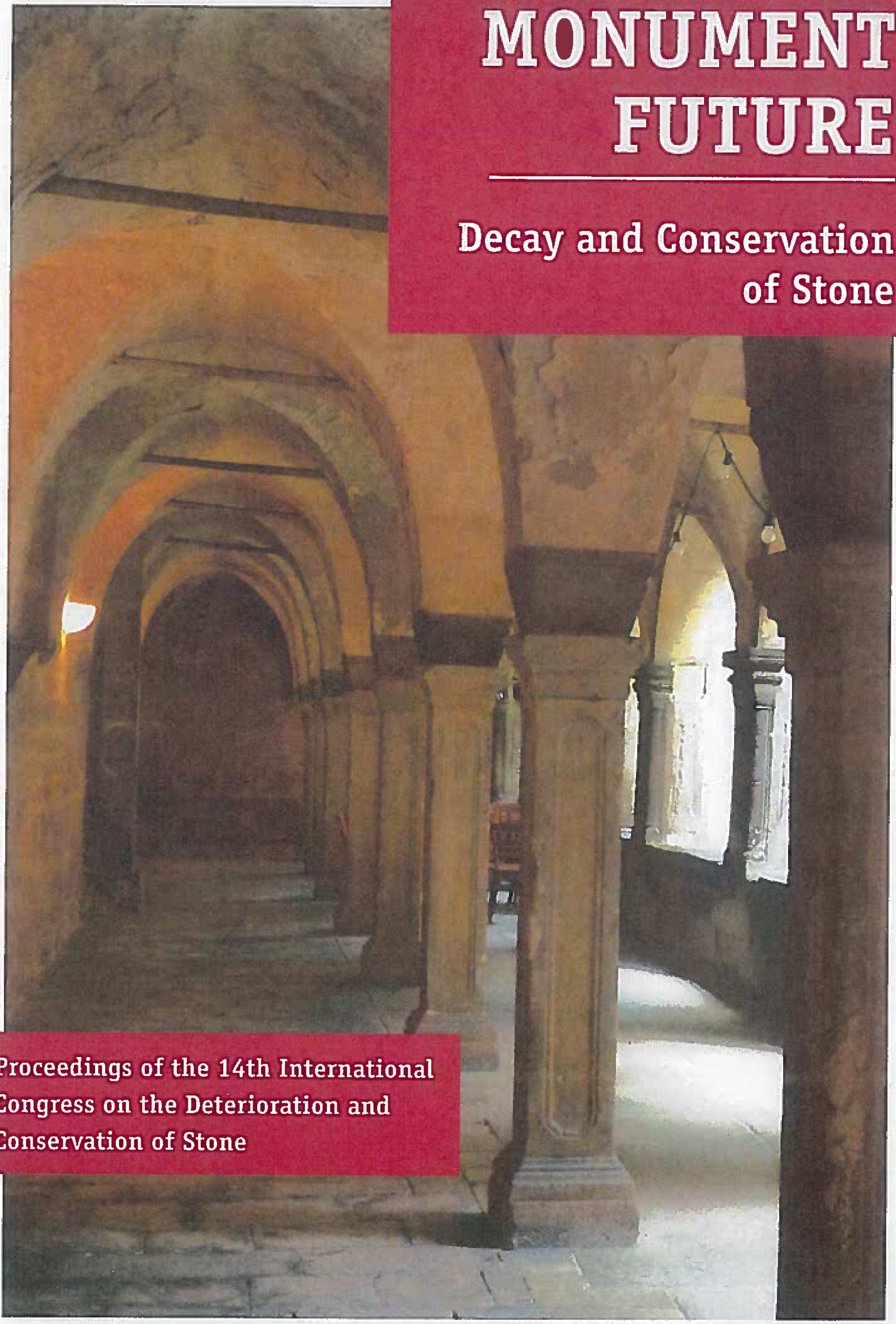
MONUMENT FUTURE

Decay and Conservation of Stone



Proceedings of the 14th International Congress on the Deterioration and Conservation of Stone

Bildnachweise der ganzseitigen Fotos: Bernhard Middendorf – S. 2; Brigitte Siegesmund – S. 4, 8, 158, 300, 392, 480, 618, 706, 1010, 1038, 1046, 1118, 1200; Carolin Pfeuffer – S. 10; Heiner Siedel – S. 790; Mathias Hueck – S. 220; Torben Fetzner and Gerd Reis – S. 968; Wanja Wedekind – S. 32, 238

„Monument Future: Decay and Conservation of Stone“ – Proceedings of the 14th International Congress on the Deterioration and Conservation of Stone, University of Goettingen and University of Kassel

Druckkosten gefördert durch die Deutsche Bundesstiftung Umwelt (AZ 34720/01)

Umschlagabbildungen: Kreuzgang im ehemaligen Kloster Schulpforta bei Naumburg von Brigitte Siegesmund

Bibliografische Information der Deutschen Nationalbibliothek
Die Deutsche Nationalbibliothek registriert diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten im Internet unter https://d-nb.de.

1. Auflage

www.mitteldeutscherverlag.de

Gesamtherstellung: Mitteldeutscher Verlag, Halle (Saale)

ISBN 978-3-96311-172-3

Printed in the EU

IN: SIEGESMUND, S. & MIDDENDORF, B. (EDS.): MONUMENT FUTURE: DECAY AND CONSERVATION OF STONE.
– PROCEEDINGS OF THE 14TH INTERNATIONAL CONGRESS ON THE DETERIORATION AND CONSERVATION OF STONE –
VOLUME I AND VOLUME II. MITTELDEUTSCHER VERLAG 2020.

AN EVALUATION OF SHELTER COATS FOR THE PROTECTION OF OUTDOOR STONES

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Abstract

Climate change and air quality are impacting the way carbonate stones deteriorate in outdoor environment. The development of new materials and techniques to protect stones outdoors is a vivid part of research. However, the evaluation of existing measures to protect cultural heritage made of stone is lacking systematic research. This study aims to understand the efficiency and compatibility of different shelter coat systems applied on monuments made of carbonate stones in Austria. For this purpose slabs of a calcarenite were covered with 10 different coatings, one half of each subsequently treated with a water-repellent, and then exposed outdoors. The alterations in the course of weathering are monitored and documented annually by photography, tests of water absorption, material loss and gloss measurements. Cross sections were analysed before exposure and repeated on regular basis to further evaluate changes, with a focus on micro-structure and the interface between stone and coating: Polarized Light Microscopy (PLM), Scanning Electron Microscopy (SEM) as well as Fourier-transform infrared (FTIR) spectroscopy for chemical alterations. The visual and photographic inspections record microbiological colonization, tendency to soiling and specific patterns produced, as well as the weathering of the coating itself. While changes in water absorption may indicate a partial loss of effectiveness, FTIR and SEM analyses show possible chemical and physical degradation of the coatings. This combination of analytical methods proved useful to understand the functionality through the key physical parameters of the coatings and determine their condition and durability. This research assesses the different protection approaches from the past and identifies materials and maintenance strategies that can be recommended for the future.

Introduction

Carbonates have always been prone to chemical and physical weathering, but as climate and air quality change, especially in relation to the rising CO_2 concentration in the air, the solubility of calcium carbonate increases (Bonazza et al. 2008) and the need for protection of outdoor stone objects becomes increasingly important. There are various possibilities to address the problem, and a great deal of research has been concentrating on newly engineered coating materials for protection, primarily in form of water repellents with functionalized surfaces (Gherardi et al. 2018). More traditional approaches to the problem can be identified in Austria, namely, the use of shelter coats which seem to be most promising for outdoor sculpture. The early uses of shelter coats, primarily related to lime-based systems with an addition of aggregate, can be found in England as part of the "lime method" (Durnan 2006, Fidler 1995). In Austria the understanding of shelter coats further broadened to include any kind of coating that contains a certain amount of aggregate (mostly sand) but, unlike mortar, can be applied by brush (Ban et al. 2018). The principal idea behind the use of shelter coats is to shift the weathering horizon, both in chemical and physical terms, from the stone surface to the surface of the coat. While the theory of material compatibility states similar petrophysical properties to the substrate as imperative (Snethlage 2011), another, often contradictory aspect regards the prevention of water uptake from the atmosphere. Above all, the durability of a coating treatment including its esthetic appearance upon weathering are additional factors of relevance.

The use of lime based shelter coats was promoted by the Federal Monuments Authority Austria (BDA) in the eighties and nineties of the last century, involving the use of silanes and/or siloxanes to further impregnate the shelter coat itself, in order to make it water-repellent and therefore longer lasting. This "Austrian approach" was introduced by H. Paschinger, the late chief chemist at the laboratories of BDA (Koller et al. 1996). Particularly, in the east of Austria such shelter coats are frequently used since then. Over time different recipes evolved; some even containing cement, silicate and/or silicon resin as primary binder. This resulted in a confusing terminology and a guideline was needed. Therefore, a working group of experts from the field was established in 2010 to produce guidelines for the use of shelter coats (Ban et al. 2018). While working on the document, many questions arose, and the need for a comparable long-term evaluation of shelter coats crystallized (Pintér et al. 2020). Thus, a field exposure program was established using 10 different recipes which were applied on slabs of calcarenite (St. Margarethen, Austria) and exposed outdoors (Tupi 2017). The evaluation of the slabs is done by students and staff of the University of applied Arts Vienna on annual basis. The field exposure site is additionaly used as a test ground by other interested scientists and practitioners in the field.

Preparation and field exposure

A total of 10 slabs (40 × 40 × 4 cm) were coated each with different formulations of shelter coats. Besides the use in the practical stone conservation, important criteria were the expected material compatibility with the stone and/or the prevention of water uptake. A complete description of the coatings and details of the recepies used are listed in Table 1. All coats were applied in three successive layers using a brush. After one month of curing, half of each slab 1–9 was additionally treated with a water-repellent (Funcosil SNL, Remmers, Germany). After another month, the slabs were exposed to the outdoor environment. They were mounted by two aluminum rails on a west facing outer wall in the chartreuse of Mauerbach in Lower Austria. The exposure enables rainwater to wash down the slabs and it facilitates strong soiling, typical for rural surroundings, consisting of organic matter and earth as well as biological colonization.

Test results before exposure

Prior to exposure, tests and analyses were performed in order to characterize the unweathered coatings. Four measurement methodes were used to assess the water absorption and the wettability of the surfaces: capillary water uptake (BS EN 15801:2009), contact angle (BS EN 15802:2009), contact sponge (Vandevoorde et al. 2013) and the droplet method (Bläuer et al. 2014). The brush method (Kirchner, Zallmanzig 2010) was used to assess the loss of material, the gloss was measured with a gloss meter. Thin-section (PLM) and scanning electron microscopy (SEM) was used to assess the microstructure of the coating itself and its interface to the stone. Water absorption tests showed that, compared to the uncoated stone, all shelter coats reduced the water absorption coefficient of the surface to some extent. The additional treatment with water-repellent strongly reduced the absorption further. The highest absorption is shown by the pure lime and the Roman cement coatings. As expected, the lowest water absorption was measured for the silicone-based shelter coat and the water-repellent treated surfaces of slabs 1–9. The results of contact angle tests, measured for the coated surfaces without additional water-repellent application, supported those obtained by contact sponge and droplet method. According to these results, the pure lime (1) and the Roman cement (8) proved to be highly hydrophilic, precluding the measurement of the contact angle. The lime-based coats with addition of acrylic dispersion (2), or white cement (3), as well as the dispersed lime hydrate (6) and the nanolime (7) produced slightly hydrophilic coatings (contact angle 30–60°), while the addition of casein to lime (5), as well as the silicate/waterglass (9) revealed slightly hydrophobic coatings (100/105°). The addition of linseed oil to lime (4), the silicone-based coating (10) and all of water-repellent treated surfaces resulted in strongly hydrophobic layers (120–135°). Gloss measurements showed that all coatings were rather matt (gloss value 0.22 GU) due to their relative roughness; they were also resistant to abrasion by brush in unweathered state (Kirchner, Zallmanzig 2010). PLM and SEM investigations of the samples taken from the slabs before exposure allowed for the following observations: the coating with lime-casein (5) showed numerous spherical air voids on the interface between the coat and the stone slab (Fig. 1a). These are so frequent that they seem to be interconnected and, upon weathering, may result in detachment or rapid wear-off. All lime-based coatings (1–7) show different amounts of

Table 1: Recipes of the applied shelter coats, results of the contact angle measurements on the fresh and not additionally treated surfaces as well as observations after one year of exposure.

No.	Short reference	Shelter coat recipe	Contact angle, before weathering	Observations after one year of exposure
01	Pure lime	1 Vol. Part Lime Putty 1 Vol. Part St. Margarethner 0–1mm	Completely hydrophilic	Very strong homogenous soiling, some decay.
02	Lime with acrylic dispersion	1 Vol. Part Lime Putty 5 wt% (binder) Primal SF016 (Rohm & Haas, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (60 °)	Homogeneous, moderate soiling. No defects.
03	Lime with white cement	1 Vol. Part Lime Putty 5 wt% (binder) white cement (Dyckerhoff, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (30 °)	Homogeneous, moderate soiling. No defects.
04	Lime with linseed oil	1 Vol. Part Lime Putty 5wt% (binder) cold pressed linseed oil, (Schmincke, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophobic (120 °)	Patchy discoloration of the surface, defects in the shelter coat.
05	Lime with casein	1 Vol. Part Lime Putty 5 wt% (binder) casein, (deffner & Johann, Germany) 1 Vol. Part St. Margarethner 0–1mm	Slightly hydrophobic (100 °)	Extremely strong soiling, strong biological colonization and decay.
06	Dispersed lime hydrate	1 Vol. Part CalXnova (dispersed lime hydrate, deffner & Johann, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (50 °)	Homogeneous moderate, soiling. No defects.
07	Nanolime	1 Vol. Part CaLoSil E50 (IBZ-Salzchemie, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (50 °)	Strong decay of the shelter coat.
08	Roman Cement	1 Vol. Part Roman cement (Rapido, Cemento Natural Tigre, Spain) 1 Vol. Part St. Margarethner 0–1mm	Completely hydrophilic	Strong soiling, no defects due to weathering.
09	Silicate	1 Vol. Part Silin AZ Fixativ (Silin, Germany) 1 Vol. Part St. Margarethner 0–1mm	Slightly hydrophobic (105 °)	Very light soiling, no decay.
10	Silicone	1 Vol. Part color LA colorless, (Remmers, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophobic (135 °)	No soiling, no decay.

cracks perpendicular to the surface, typically attributed to shrinkage (Fig. 1b).

The frequency of this kind of cracks seems to be the lowest in the samples from the slabs with acrylic dispersion (2) and linseed oil (4), in the lime coating. The latter additionally shows long thin cracks running parallel to the surface (Fig. 2a) which would possibly result in accelerated decay (Fig. 2b). The dispersed lime hydrate coating (6) shows few and small cracks, while the one with nanolime (7) is thin and highly porous with few micro cracks. The Roman cement coating (8), though highly absorbant, has no cracks at all.

Test results after one year of exposure

For the periodic evaluation of the performance of the coats, a combination of non-destructive and micro destructive methods was employed. While documentation and in-situ tests will be repeated each year (photographic documentation, water absorption using contact sponge and droplet method, gloss measurements etc.), laboratory tests will be carried out less frequently, depending on the expected relevance. They include analyses of polished thin-sections by PLM as well as SEM, and FTIR. Tests of the capillary water uptake in the laboratory and measurements of the contact angle will be repeated every two to three years.

After one year of exposure, there are already some results that deserve to be published at present. Most of them are related to the visual examination of the slabs and are confirmed by PLM and SEM.

The visual inspection of the slabs yields the following observation: soiling of the surfaces is generally intense. The surfaces without water-repellent (halves of slabs 1–9) are in general soiled to a much higher degree as compared to the water-repellent treated and the silicone based coats (10). The latter can be explained by the hydrophobic properties even though the roughness seems to be the highest of all coatings. Amongst the lime-based coats, the one with casein additive (5) shows by far the strongest soiling and microbiological colonization; in this case both the half with and without water-repellent are concerned (Fig. 3b).

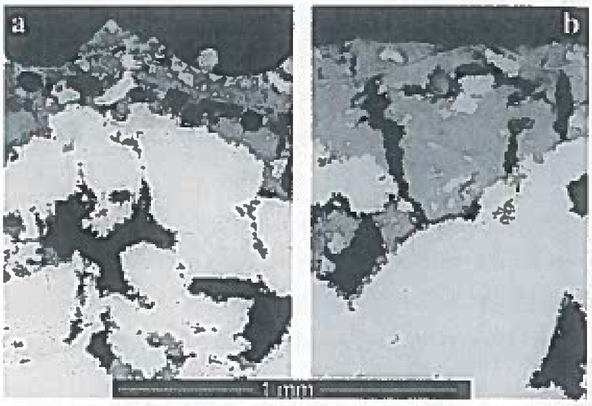

Figure 1a + b: SEM-BSE images of cross-sections from surfaces coated with (a) lime-casein and (b) pure lime.

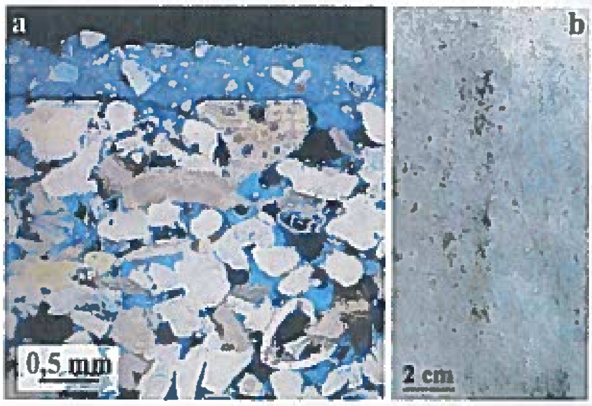

Figure 2a + b: Lime-linseed oil coating with tendency to detach; visible by PLM before exposure (a), resulting in surface flaking after one year of exposure (b).

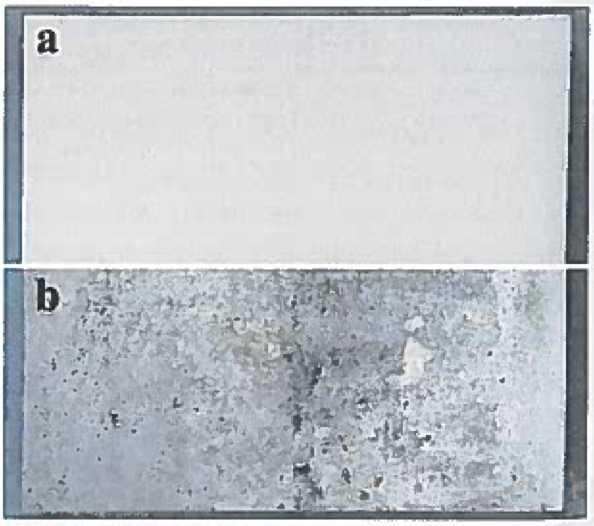

Figure 3a + b: Slab with lime-casein coating (left half with hydrorepellent) before (a) and after one year of exposure (b).

It can be argued that the microbiological activity is facilitated by the protein available in the coating. Also the lime coat with linseed oil (4) shows patchy and unaesthetic discoloration after one year of exposure. The pure lime has a strong but evenly distributed soiling. Both additions of acrylic dispersion (2) as well as of white cement (3) prove to exert a positive effect by lowering the soiling tendency of lime-based coatings. The modern lime-based shelter coats performed very differently from each other. While the nanolime-based coat (7) was almost completely weathered off, the coat based on dispersed lime hydrate (6) performed very well in terms of both weathering resistance and the tendency to soiling. The Roman cement-based coat (8) shows a strong soiling similar to the one of the pure lime; this might be due to its high porosity, roughness and hydrophilicity. Both silicate- (9) and silicone- (10) based coats reveal almost no soiling and no weathering at all. In these cases, results from the coming years might be of greater interest, especially regarding their weathering patterns.

The micro-analyses on cross sections of samples taken after one year of exposure confirm the macroscopical observations, and allow a preliminary evaluation of the durability of the lime-based coatings and predictions for the coming years. The results show that early weathering of the pure lime coat (1) is visible in SEM: the carbonate skin starts to show signs of degradation. The recipes with acrylic dispersion and cement seem to be more durable and show fewer changes in the surface texture after the first year of exposure.

Discussion

When evaluating the pros and cons of a shelter coat system by its properties, one must get back to the question of the expected role of such a coating, i. e. a protective, a sacrificial or rather an esthetic function. We believe that there is no universal answer to this question, though the principles of conservation must always be granted, e. g. the primacy of the original against the service life of a later surface coat. Thus, both the sacrificial and the protective role of a shelter coat may contribute to prolonging the life span of the object. However, whilst the latter aspect favors the physico-mechanical similarity between a coat and its substrate, e. g. in terms of porosity and absorptivity, the former rather supports the idea of the coating to be water repellent in contrast to the substrate. The question which approach is better can only be answered in view of the conditions of exposure and the properties of a given stone monument without neglecting the coating's durability and appearance. In addition to these general considerations, the exposure site presented, yields important insights which will become more significant in the course of further monitoring.

For the lime-based shelter coatings, the addition of acrylic dispersion or white cement (5wt% of the binder) showed a reduced soiling tendency and good durability. The dispersed lime hydrate coat also performed very promising. The addition of casein and linseed oil increased the tendency to soiling and microbiological colonization and seem to lower durability. The nanolime coat has a very low durability due to the low lime content in the product used, and the low thickness of the layer. Other nanolime formulations might be more suitable for this kind of task and should be tested in future. The Roman cement is strongly soiled presumably due to its rough surface along with the high porosity in favor of water absorption; this coat can thus be considered compatible to porous stone substrates but does not protect against precipitation or soiling. The silicate and silicone resin coats show almost no changes after a year of exposure, neither soiling nor signs of weathering. They can be considered least compatible in respect to the porous limestone because of their silicate nature and the water repellency, respectively, possibly resulting in a risk for the stone on a long-term perspective. Similar considerations apply to the halves of slabs 1–9 treated with hydrorepellent. With the exception of the lime coat with casein addition, they show drastically less soiling and weathering effects.

This small scale study reveals different trends and answers some of the questions posed. In order to fill the knowledge gaps regarding shelter coats, more research has to be conducted including laboratory tests and artificial ageing.

Summary

Shelter coats have been sucessfully used in different countries for some decades. Despite mostly positive experiences, little research has been done in this field. Since 2010, shelter coats have been the focus for conservators and heritage scientists in Austria (eg. Ban et al. 2018). A field exposure series was triggered by this debate and installed in Mauerbach, Lower Austria. Tests and analyses before and after one year of exposure were made and are presented in this paper. Some trends can already be observed. All shelter coats reduce the water absorption of the surface in case of the porous limestone of St. Margarethen. The additional water-repellent treatment reduces the water absorption further, as expected. Among the lime-based coats, the ones with addition of acrylic dispersion and white cement as well as the coats with dispersed lime hydrate show the lowest tendency to soiling, highest durability and esthetically acceptable soiling pattern. The Roman cement coat is subject to strong soiling, probably due to its rough and, absorbent surface. The silicate and silicone coats show almost no change after one year; results from the coming years will provide further insights. Finally, the hydrophobic treatment of the coats as proposed by H. Paschinger seems to increase the durability and delay soiling, however results of prolonged monitoring will be of great interest.

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