Article

Limewashes with Linseed Oil and Its Effect on Water and Salt Transport

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Abstract: Paints are the protective and aesthetic skin of buildings, so (re) painting is one of the most recurrent maintenance actions. Limewashes have been used since antiquity and are currently of high interest for both conservation and new construction, majorly thanks to their eco-friendly and antiseptic features, and ability to improve the performance of the materials in relation to water transport. Linseed oil is a traditional water-repellent additive that can enhance the water-shedding properties of the limewashes. However, it has the risk of altering the drying kinetics of the substrate if an improper dosage is used. In this work, limewashes with the addition of varying dosages of linseed oil have been applied on two types of natural stone to study the effect of the paints in respect to water and salt transport. The water absorption by capillarity was reduced in both stones coated with pure limewash and limewash with oil, while the drying rate was slightly accelerated. The effect of the paints on the drying of the salt-laden stones varied. The salt damage developed during drying also diverged in both stones, damaging the coats and stone surface of the less porous stone and mainly promoting salt efflorescence in the most porous one.

Keywords: lime paint; coating; vegetable oils; capillarity; drying

1. Introduction

Limewashing was one of the most widespread techniques for indoor and outdoor wall covering since classical times. Limewashes became popular mainly thanks to lime availability, aesthetic and antiseptic properties. In Europe, limewashes were typically reapplied annually during spring. Beyond a maintenance intervention, it was also a social practice transmitted from generation to generation [1]. However, with the establishment of the paint and coating industry following the industrial revolution, these materials were progressively replaced by synthetic ones, even though their compatibility with traditional materials and cost-effectiveness were not proven to be better. In fact, many of these synthetic paints later proved to trigger dampness problems, the onset of several damage mechanisms, mainly by blocking the drying of the porous materials on which they were applied [2]. Moreover, certain chemicals used to manufacture these paints are hazardous to the environment. These aspects have recently brought the scientific community to rediscover traditional materials.

On the one hand, traditional recipes have the long-term seal of quality regarding compatibility and green credentials. On the other hand, they are outdated to face the rising severity of weathering agents assigned to climate change (e.g., wind-driven rain, floods, humid-dry cycles). Therefore, further efforts are required to improve the durability of new building materials, not only for conserving our heritage but also for new constructions made of porous materials (e.g., earthen-based constructions).

Limewash is an aqueous suspension of calcium hydroxide that usually contains ca. 15–20 wt.% of calcium hydroxide and 80–85 wt.% of water, which gives it a consistency

similar to that of whole milk [3]. Limewash can be made from lime putty or dry hydrated lime (powder) by adding water. However, according to Schofield [4], limewash made with powder has lower quality than that prepared with putty. Mold and Godbey [3] recommend applying at least three to five coats of limewash to achieve sufficient coverage of typical porous building materials; several applied coatings of a thin limewash will create a more durable finish than fewer and thicker coats. The limewash is translucent after application but becomes opaque after drying. The appearance of the final finishing is matt, porous, and permeable to water.

The main advantages of using limewashes in the conservation of old buildings' facades are with its compatibility with the original porous materials thanks to its high water vapour permeability and water-shedding properties, antiseptic features that hinder biocolonization, and the preservation of the traditional aesthetical image of the building [3–5]. The main drawbacks related to the use of limewashes in exterior walls are its low durability towards rain, high soiling retention, and reduced washing resistance, thus demanding frequent maintenance, especially in polluted areas rich in sulphurous gases [5].

A way to overcome limewashes' durability issues related to weathering agents involving water transport is by incorporating additives that grant water-repellence properties. Vegetable oils and animal fats were the most common water-repellent additives used in paints, stuccos, and mortars [6]. The ground for the choice of the lipid depended on the regional availability. Linseed oil was commonly used from ancient times in many regions of Europe [7]. Talafierro [8] has made a comprehensive literature review of historic limewash recipes in the United States, some of which first published in Europe. The author mentions recipes with linseed oil disseminated in Britain and France in the 19th century [8]. In the Czech Republic, linseed oil was used in the Renaissance and Baroque époques to prepare limewashes with water-shedding properties [9].

Such materials were used in structures exposed to the severe action of water, e.g., walls facing wind-driven rain, pavements, baths, aqueducts [6,7,10–12]. However, the technical information about the techniques, materials, and tools is scarce. The preparation procedure and amount of additive play a key role in the properties and performance of the material, e.g., if the paint or mortar has too high water-repellence, it may defeat the purpose of improving the protection of the substrate as it may worsen dampness problems by supressing the drying of the underlying substrate [2,4,13]. Ancient constructions usually have thick walls made of porous hydrophilic materials in direct contact with the ground. As a result, walls are frequently damp and contain soluble salts accumulated throughout time. Therefore, in this case, it is important to study the influence of water-repellent coats on the drying of materials also have in the presence of soluble salts.

The main goal of this study is to determine the optimal amount of linseed oil for granting water-repellence to limewash while maintaining similar drying properties to the pure one. Following the study by Gonçalves and Brito [14] with pure lime paints, this study also aims to analyse how the drying kinetics vary in the presence of a salt solution instead of pure water, and how do the different limewashes change the degradation patterns formed during drying of salt contaminated samples. This paper aims to answer the following research questions:

- How do the water absorption and the drying kinetics of two types of porous systems vary with limewash coatings with an increasing amount of linseed oil?
- How do the drying kinetics of the limewashed porous substrates vary in the presence of a salt solution instead of pure water?
- How do the limewashes influence the development of salt efflorescence or degradation during drying of the salt-laden substrates?

2. Materials and Methods

2.1. Materials

2.1.1. Lime Putty and Linseed Oil

Lime putty of class CL 90 according to EN 459-1 [15] supplied by Carmeuse (Vápenka Mokrá, Mokrá, Czech Republic) was used to prepare the limewashes. The lime putty was prepared by mixing the hydrated lime powder with water in a ratio (wt.) 1:1.2 with an automatic mixer for 1 min at a speed of 10 min/s; the putty was then stored for one year before using; the average amount of water in the lime putty after decanting was 55 ± 2 wt.%. The amount of water in the putty was determined gravimetrically after drying decanted portions of ca. 50 g of putty (3 replicates) at 60 °C until constant mass.

The particle size distribution of the lime putty was measured by static laser scattering using Cilas 920 particle size analyser, which can measure the particle diameter within the range of 0.3–400 μm. The particle size was determined on a 1 cc specimen of lime putty. The results showed that 90% of the volume frequency of the lime particles had ca. 43 μm diameter, 50% had 15 μm diameter, and 10% had 2 μm diameter.

Raw linseed oil (GRAC s.r.o., Prague, Czech Republic) extracted by the cold press method was used in this study. The fatty acid composition of the oil has been previously determined [16]; it is composed of 54 wt.% of linolenic acid (C18:3), 20% of oleic acid (C18:1), 16% of linoleic acid (C18:2), 6% of palmitic acid (C16:0) and 4% of stearic acid (C18:0). It is a very chemically reactive oil because it contains a high amount of linolenic acid (three double bonds) that promotes the fast polymerization of the oil. Therefore, even nowadays is commonly used in paints and varnishes. Linseed oil grants water-repellent properties to lime via chemical reaction of the triglycerides present in the oil with calcium hydroxide. The triglycerides are not chemically stable in the high alkaline environment of a calcium hydroxide suspension and hydrolyze to glycerol and fatty acid anions. The fatty acid anions then react with calcium hydroxide to form hydrophobic calcium salts [16]. The amount of oil determines the amount of hydrophobic reaction products and, hence, the degree of water-repellence. If an excessive oil dosage is used, the degree of water-repellence may become too high and suppress the drying of the porous materials. Therefore, different oil dosages were tested in this study (1, 1.5 and 3 wt.% in respect to the lime weight) to determine which amount of oil can be added to the lime paint without compromising the breathability of the substrate.

2.1.2. Preparation of the Limewashes

The limewashes were prepared by manually mixing raw linseed oil (GRAC s.r.o., Czech Republic) with lime putty (after decanting) with a spoon and afterwards adding water to achieve a suspension containing 20 wt.% of lime and 80 wt.% of water. Linseed oil was added in 1, 1.5 and 3 wt.% in respect to the weight of lime in the putty, i.e., excluding the water content. Before and during painting, the limewashes were regularly mixed to ensure a homogeneous suspension of lime particles in each brushing step. Pure limewash (without linseed oil) was prepared in the same way to use as a reference. Specimens without limewash were also prepared to use as uncoated reference.

2.1.3. Substrates

Two types of natural stone from the Czech Republic widely used in the country's architectural heritage were selected for this study: a sandstone locally known as Mšené and a marlstone known as Opuka. Besides their heritage importance, these stone types were selected because they have a very different behaviour regarding water transport, an important aspect for assessing the performance of the limewashes.

Mšené stone, commonly known internationally as Prague sandstone, is quarried nearby Mšené-Lažně, a town about 40 km from Prague, and has been used in buildings and sculptures since the 14th century. Mšené is a fine-grained calcite-argillaceous sandstone of grey colour with yellow-brown stains. The features of this stone, namely its homogene-

ity, high porosity and unimodal pore size distribution, lead researchers to use it in salt crystallization research studies, e.g., [17–19].

Opuka is a sandy marlstone quarried in the vicinity of Prague and was largely used in buildings and sculptures mostly from the 9th to the 14th century in the Bohemian region [20]. In this study, the variety commonly known as Gold Opuka was used. It is a very fine-grained stone mainly composed of silica, calcite, and clay; it has yellow-beige colour and shows visible bedding planes.

The physical characteristics of the stones relevant to the present study are summarized in Table 1. The properties were determined in a previous work [21] using specimens of the same stone blocks.

Table 1. Porosity, bulk density, and main pore size of the stones [21].

Stone	Stone Code	Open Porosity [1] (%)	Bulk Density [1] (kg·m^{-3})	Main Pore Size [2] (µm)
Mšené	MS	33.3 (±1.4)	1899 (±39)	27
Opuka	OP	23.6 (±1.4)	2037 (±41)	0.2

[1] According to [20]. [2] Determined with mercury intrusion porosimetry.
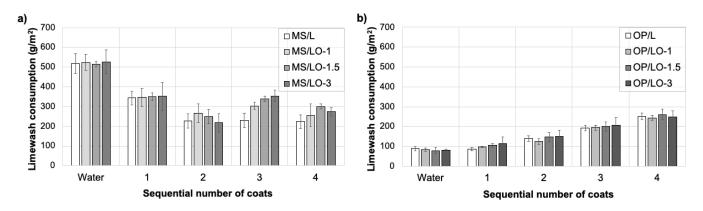
2.1.4. Application of the Limewashes

The stone cubes of 50×50 (±2) mm were sealed with epoxy resin on four surfaces, leaving two opposite sides unsealed. Opuka stone bedding planes were oriented parallel to the exposed surfaces. The stone specimens were dried at 60 °C, and the dry mass was registered. The limewashes were applied with a brush of soft-to-medium stiff bristles on one of the unsealed surfaces of the specimens. Each stone's surface was wetted with pure water with a brush just before applying the first layer of limewash. Four paint layers were applied crisscrossed with an interval of 24 h between each one. During the application and throughout the curing period of 60 days, the specimens were stored in a chamber at 20 ± 5 °C and 60 ± 5% relative humidity (RH) with ca. 500 ± 100 ppm CO_2. Each limewash type was applied to four specimens of each stone. In the case of the stones treated with limewash with linseed oil, the first two coats correspond to pure limewash to provide the base and adhesion to the substrate, following the recommendation from Mold and Godbey [3]; the third and fourth coats correspond to limewash with linseed oil. Table 2 lists the type of the specimens prepared and their respective code used henceforth to identify the specimens.

Table 2. Identification of the type of specimens prepared.

Stone	Limewash Type	Specimen Code
Mšené	Without limewash	MS/R
	Pure limewash	MS/L
	Limewash + 1% oil	MS/LO-1
	Limewash + 1.5% oil	MS/LO-1.5
	Limewash + 3% oil	MS/LO-3
Opuka	Without limewash	OP/R
	Pure limewash	OP/L
	Limewash + 1% oil	OP/LO-1
	Limewash + 1.5% oil	OP/LO-1.5
	Limewash + 3% oil	OP/LO-3

2.1.5. Testing Procedures

The limewash uptake by each stone type was assessed gravimetrically. Before applying the first coat of limewash, the stone surface to be treated was wetted with pure water with a brush. Afterwards, the weight of the wet stone specimen was registered. Next, the first coat of limewash was applied, and the specimen was weighed again. The limewash consumption was calculated, and the results are shown in Figure 1.

Figure 1. Limewash uptake between coats: (**a**) Mšené, (**b**) Opuka. Note: the samples are wetted with water just before applying coat no.1; coats nos. 1 and 2 correspond to pure limewash (L) in all specimens.

The contact angle of the limewashed surfaces with water drops was used to check the wettability of the coats. A drop of 20 ± 5 μL of water was poured from a 50 mm distance onto the specimen's top surface, and a microphotograph was taken with a binocular microscope. After 10 s the drop hit the surface. The angle of the drop of water to the surface was then calculated by image analysis. Measurements were performed in four replicates for each stone and limewash type, and the results are given in Table 3.

Table 3. Values of contact angle with water drops, water absorption by capillarity coefficient, drying rate, and drying index (average of 4 specimens $\pm$ standard deviation).

Specimen	Contact Angle	Capillarity Coefficient $(kg \cdot m^{-2} \cdot h^{-1/2})$	Capillarity R^2	Drying Rate Water $(kg \cdot m^{-2} \cdot h)$	Drying Rate Salt $(kg \cdot m^{-2} \cdot h)$
MS/R	*	36.28 ($\pm$1.96)	0.99	0.23 ($\pm$0.03)	0.08 ($\pm$0.01)
MS/L	*	19.25 ($\pm$2.78)	0.95	0.28 ($\pm$0.02)	0.16 ($\pm$0.05)
MS/LO-1	28 ($\pm$11)	13.20 ($\pm$0.84)	0.95	0.28 ($\pm$0.01)	0.08 ($\pm$0.01)
MS/LO-1.5	34 ($\pm$6)	5.27 ($\pm$0.46)	0.96	0.29 ($\pm$0.00)	0.08 ($\pm$0.03)
MS/LO-3	70 ($\pm$4)	0.66 ($\pm$0.05)	0.99	0.26 ($\pm$0.02)	0.06 ($\pm$0.01)
OP/R	*	2.09 ($\pm$0.05)	1	0.19 ($\pm$0.01)	0.054 ($\pm$0.003)
OP/L	*	1.88 ($\pm$0.04)	0.99	0.22 ($\pm$0.02)	0.053 ($\pm$0.006)
OP/LO-1	25 ($\pm$3)	1.76 ($\pm$0.13)	1	0.20 ($\pm$0.03)	0.052 ($\pm$0.006)
OP/LO-1.5	29 ($\pm$3)	1.74 ($\pm$0.04)	1	0.20 ($\pm$0.01)	0.051 ($\pm$0.003)
OP/LO-3	85 ($\pm$6)	1.35 ($\pm$0.06)	0.99	0.20 ($\pm$0.02)	0.046 ($\pm$0.003)

* The material absorbed the water drop within 10 s after the drop hit the surface.

The water absorption by capillarity was performed according to the RILEM recommendation [22] with four replicates of each specimen. The water absorption by capillarity curves of the most representative specimens are given in Figure 2, and the coefficients calculated from the curves are shown in Table 3.

The drying test was determined according to the RILEM recommendation [22] with four replicates of each stone and limewash type. The specimens were saturated with pure water by capillarity through the bottom surface (i.e., untreated surface) until reaching constant mass. Afterwards, the bottom surface was sealed with parafilm, and the specimens were left to dry only through the top (treated) surface in a room at constant thermohygrometric conditions (20 °C, 50% RH). The drying conditions were monitored with thermohygrometers placed close to the specimens and registered a variation of 20 ± 3 °C and 50 ± 7%.

All samples were tested at the same time in the same acclimatized room. The drying curves with pure water are given in Figure 3, and the respective drying rate values calculated from the curves are given in Table 3.
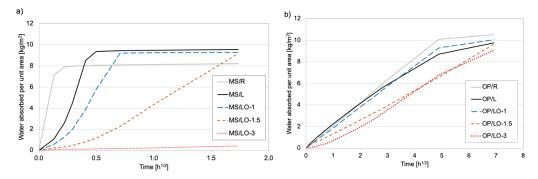

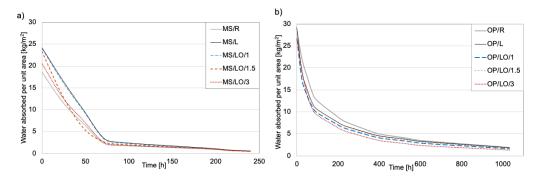**Figure 2.** Water absorption by capillarity curves of (**a**) Mšené and (**b**) Opuka.
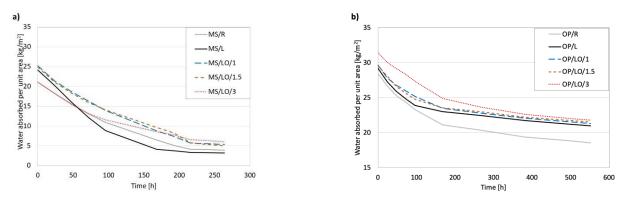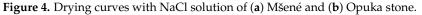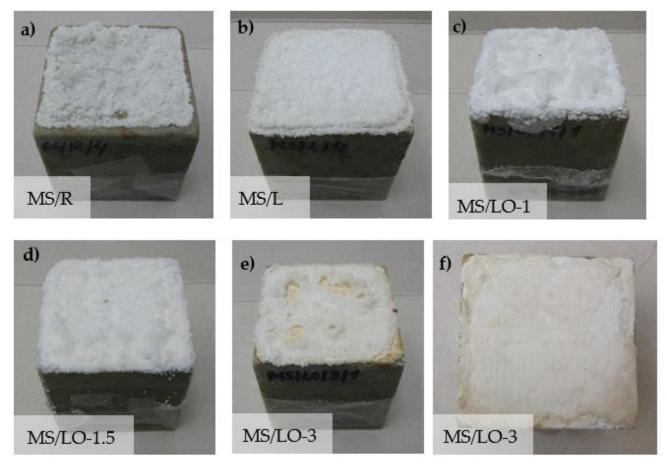

Figure 3. Drying curves with pure water of (**a**) Mšené and (**b**) Opuka stone.

The same specimens used for the drying test with pure water were saturated by capillarity with a sodium chloride (NaCl) solution. Sodium chloride was selected because it is a common salt detected in ancient buildings worldwide. Though NaCl is more common in buildings located in coastal areas, it can also be present in regions far from the sea where water frequently freezes during winter, due to its long-term use as a de-icing agent. A sodium chloride solution with a concentration required to introduce 1 wt.% of salt in each stone type in respect to its dry weight was used. This concentration was chosen based on the highest typical NaCl content detected in porous building materials according to the KIK-IRPA salt database [23]. Hence, a salt solution concentration of 11.6% was used for Mšené stone, and 26.0% was used for Opuka stone. The salt solution was prepared by dissolving the required amount of NaCl (ACS reagent > 99.0%) in pure water at ca. 20 °C. The specimens were saturated by capillarity through the bottom surface (uncoated). Afterwards, the bottom side of the specimens was sealed with parafilm. A transparent film extended 5 mm above the top surface of the specimens was placed around the specimens to avoid salt efflorescence or material debris, developed during the test, from falling. The specimens were left to dry under the same conditions as those dried with pure water. The drying curves of the samples with NaCl solution are given in Figure 4, and the respective drying rate values calculated from the curves are given in Table 3. The alterations observed in the specimens during drying were monitored daily, and photographs of the specimens at the end of the test are shown in Figures 5 and 6. At the end of the test, the salt efflorescence and debris formed during drying were brushed from the exposed surface, and its weight was measured. To distinguish the mass of salt from that of debris (paint layer and stone), the brushed material was diluted in ca. 100 mL of pure water, then filtered, and the mass of insoluble material was determined after drying to a constant mass at 60 °C. Figure 7 shows the mass of salt and debris registered for each stone.
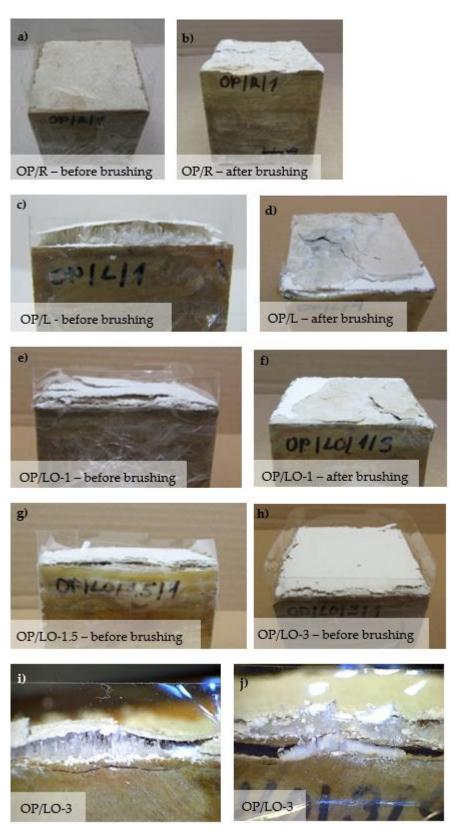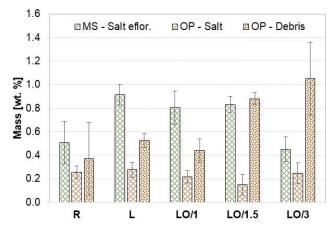
Figure 4. Drying curves with NaCl solution of (**a**) Mšené and (**b**) Opuka stone.

Figure 5. Mšené specimens at the end of the drying test after saturation with 1 wt.% of NaCl in respect to the specimens' weight: (**a**) MS/R; (**b**) MS/L; (**c**) MS/LO-1; (**d**) MS/LO-1.5; (**e**) MS/LO-3; (**f**) MS/LO-3 after removing the salt efflorescence.

Cross-sections of the stone specimens were prepared for analysis with a scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector (EDX) with the main aim of observing the depth of penetration of the limewashes into the stones' superficial layer. The images were collected under 15 kV voltage at a working distance of 15 mm and a high vacuum regime. For the stones coated with limewashes containing linseed oil, only those with 1.5% oil dosage were analysed. The SEM photomicrographs and respective EDX elemental maps taken in Mšené and Opuka specimens are shown in Figures 8 and 9, respectively.

Figure 6. Opuka specimens at the end of the drying test after saturation with 1 wt.% of NaCl in respect to the specimens' weight: (**a**) OP/R before brushing; (**b**) OP/R after brushing; (**c**) OP/L before brushing; (**d**) OP/L after brushing; (**e**) OP/LO-1 before brushing; (**f**) OP/LO-1 after brushing; (**g**) OP/LO-1.5 after brushing; (**h**) OP/LO-3 before brushing; (**i**) Detail of OP/LO-3 with salt efflorescence developing between the stone and the paint layer; (**j**) Detail of OP/LO-3 with salt efflorescence developing between the stone and the paint layer and between the stone bedding planes.

Figure 7. Mass of salt and debris brushed from the surface of Mšené (MS) and Opuka (OP) stones at the end of the drying test with NaCl solution. Note: only salt efflorescence formed on the surface of the Mšené stone. Opuka showed delamination of the paint layer and stone caused by cryptoefflorescence.
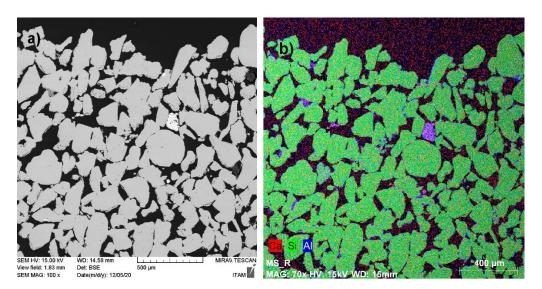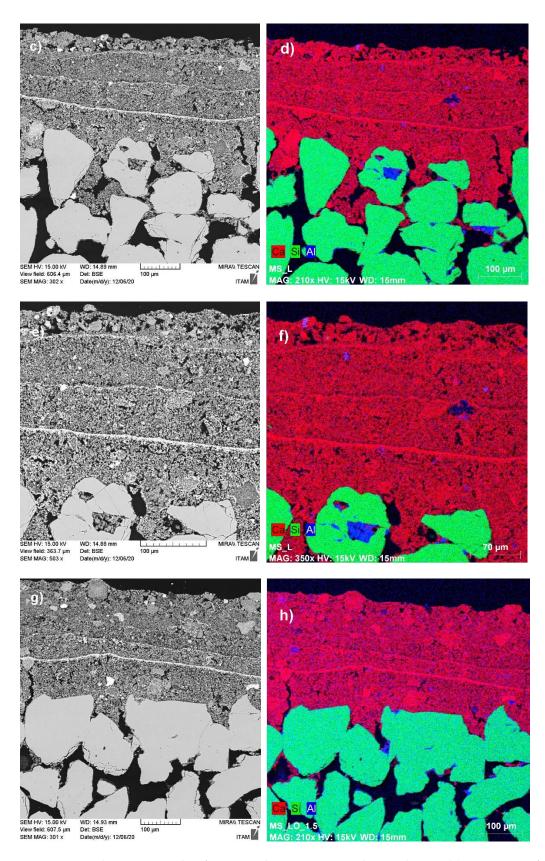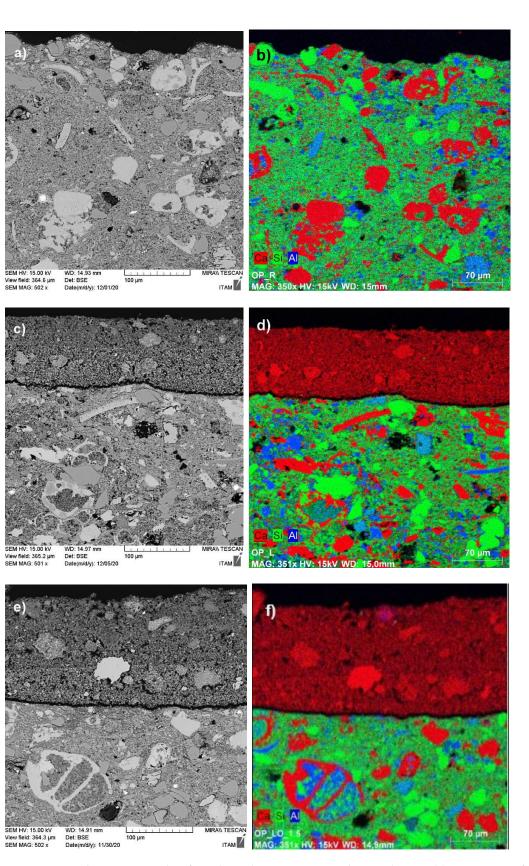

Figure 8. *Cont.*

Figure 8. SEM photomicrographs of Mšené and respective EDX elemental maps: (**a**) SEM image of MS/R; (**b**) SEM-EDX map of MS/R; (**c**) SEM image of MS/L; (**d**) SEM-EDX map of MS/L; (**e**) SEM image of MS/L showing a detail of the paint layers; (**f**) SEM-EDX image of MS/L showing a detail of the paint layers; (**g**) SEM image of MS/LO/1.5; (**h**) SEM-EDX map of MS/LO/1.5.

Figure 9. SEM photomicrographs of Opuka and respective EDX elemental maps: (**a**) SEM image of OP/R; (**b**) SEM-EDX map of OP/R; (**c**) SEM image of OP/L; (**d**) SEM-EDX map of OP/L; (**e**) SEM image of OP/LO/1.5; (**f**) SEM-EDX map of OP/LO/1.5.

3. Results and Discussion

The amount of limewash uptake is given in Figure 1. Mšené stone absorbed a higher amount of limewash than Opuka, in line with its larger pore size and porosity. Given that the most frequent lime particle size diameter is 43 and 15 μm and that the smallest size detected is 2 μm, the lime particles cannot penetrate into the pores of Opuka stone.

Mšené showed a slight tendency to absorb a lower amount of limewash in subsequent applications, in contrast with Opuka. This is probably related to the fact that in Opuka, the first lime coats do not penetrate the pore space as in Mšené, thus forming a layer at the surface that is more porous than the underlying stone. This superficial lime layer formed can contribute to the slight tendency to consume more limewash in subsequent applications. In the case of Mšené stone, the trend for limewash consumption is inversed because the stone has much wider pores. The first coats of limewash penetrate and render the superficial stone layer less porous than the stone itself, hence less prone to absorb further lime coats.

The values of contact angle with water drops, absorption by capillarity coefficient, and drying rate are presented in Table 3. Reference specimens of both stones without limewash (R) and with pure limewash (L) absorbed the water drop after 10 s the drop hit the surface. None of the stone specimens coated with limewashes with linseed oil achieved a contact angle high enough to be classified as hydrophobic, i.e., higher than 90°. Limewashes with increasing dosage of linseed oil granted similar water drop contact angles in both stones, being slightly higher in Opuka with higher oil dosages. As expected, increasing the oil dosage induces an increment in the degree of water-repellence of the limewash in both stones; this increment is more or less linear with the increasing amount of oil added.

The water absorption by capillarity curves are shown in Figure 2, and the respective capillarity coefficients are given in Table 3. There is a substantial reduction of the absorption rate in MS coated samples. Pure limewash alone (MS/L) promotes a relevant decrease in the capillary water uptake, further enhanced with increasing oil dosage. The addition of 3% of oil to the limewash renders the Mšené surface (MS/LO-3) virtually non-absorbent (Figure 2a). In the case of Opuka, the water absorption rate is considerably less influenced by the limewashes compared to Mšené (Figure 2b). However, the contact angle with water drops was slightly higher than that registered in Mšené. Pure limewash (OP/L) and limewash with 1% oil (OP/LO-1) show similar water absorption by capillarity results. Likewise, limewashes with 1.5% and 3% of oil display similar water absorption curves.

The evaporation curves with pure water are shown in Figure 3, and the corresponding drying rates are given in Table 3. The drying kinetics of materials saturated with water is divided into two stages: (i) Stage I, in which the evaporation occurs at a constant rate at the evaporative surface of the material (the water content decreases more or less linearly with time) and is dominated by capillary action, and (ii) Stage II, which starts after the critical moisture content is reached, i.e., the water capillary feeding to the evaporative surface is interrupted, and evaporation is dominated by vapour flow [24].

The effect of the limewashes on the drying with pure water was not very significant with both pure limewash and limewash with linseed oil. The drying rate was slightly accelerated by the pure limewash, which is in line with other studies on the effect of limewashes on the drying kinetics of porous materials [25,26] and is assigned to an increment of the effective surface of evaporation. Brito and Goncalves [25] explain the reason for this phenomenon: the increment in the drying rate is related to Stage I drying, in which the wet front is at the evaporative surface. This is likely related to the increment of the effective evaporative surface that lime generates during Stage I [25]. The effective surface of evaporation depends on the porous structure of the materials. Given that Mšené stone has wider pores than Opuka, the acceleration of the drying rate is more relevant because the increment of the evaporating surface with the lime paint is also higher.

As mentioned, oil addition to the limewash had little effect on the drying of both stones. In the case of Mšené, only the highest oil dosage slightly reduced the drying rate, whereas in Opuka, the increment of the oil dosage did not seem to affect the drying.

Nevertheless, the drying rate was still slightly higher with all limewashes in respect to the specimen without paint; this is in line with the results of a previous study [21].

The evaporation rate was substantially reduced in the presence of NaCl solution instead of pure water (Figure 4), as commonly observed in practice and lab [27]. This phenomenon is natural because the water activity is reduced in the presence of salt [28]. The limewashes had a nuanced effect in the drying, with a tendency for slower drying with increasing oil dosage.

The aspect of Mšené specimens at the end of the drying test with salt solution is shown in Figure 5. Salt efflorescence began appearing in all Mšené specimens around the edges after 1-day drying. After 3 days, the entire surface was covered with wet fluffy efflorescences (vitreous aspect). By day 7, the development of efflorescences halted and appeared drier (whiter). With the highest dosage of linseed oil (3%), the salt efflorescence did not develop as homogeneously and was not as evenly distributed on the surface as on pure limewash and limewash with 1 and 1.5% of oil (Figure 5e).

After brushing off the salt efflorescences, the limewashed surface of the specimens appeared sound (including the non-painted reference), except for the specimens with 3% of oil in the limewash (MS/LO/3), which appeared yellow and showed slight damage by scaling of the paint layer, especially around the edges (Figure 5f). The yellowing effect is probably due to the high amount of linseed oil, which is generally reported to be prone to yellowing due to residual conjugated double bonds, especially in oils with a high amount of linolenic acids [29], which is the case.

The aspect of Opuka specimens at the end of the drying test with salt solution is shown in Figure 6. All Opuka specimens showed damage by delamination. In the limewashed specimens, cryptoefflorescences formed between the stone and all coatings and underneath the stone bedding planes. The cryptoefflorescences formed between the stones' bedding planes corresponded to fibrous crusts composed of columnar crystals standing perpendicular on the surface (Figure 6j). The efflorescences formed between the stone surface and the paint layers were more porous and resembled whiskers. According to Zehnder and Arnold [30], fibrous salt crusts develop when the substrate is moderately humid, whereas whisker-like efflorescences form when the surface is nearly dry, in line with the drying stage in which this type of efflorescence developed. After brushing the debris composed of stone, efflorescence, and paint, the exposed surface was powdery.

Delamination and powdering is a very common deterioration pattern observed in Opuka stone onsite in the presence of soluble salts [20,31]. Therefore, the observed damage in this lab study is in line with natural exposure weathering. Laboratory salt crystallization studies encompassing both Mšené and Opuka have indicated that Opuka stone is very susceptible to salt damage [32,33], whereas Mšené is fairly resistant in comparison with Opuka [19,32].

Figure 7 shows the mass of salt and debris collected by brushing the surface of the stones at the end of the test. In the case of Mšené, only salt efflorescence was collected. In Opuka, salt efflorescence, cryptoefflorescence, paint layer, and stone were collected. A much higher amount of salt was registered in Mšené stone in comparison with Opuka; the amount of efflorescence was highest in the case of the specimens with pure limewash. According to Pavlík et al. [19], Mšené stone exhibits fast salt-transport-capability and, in the case of NaCl, salt transport is almost as fast as water. Limewash seems to enhance the salt transport to the stone's surface, thus acting as a 'desalinating medium.' This is in line with the study by Petkovic et al. [34], which showed that moisture and salt transport, and salt accumulation are favoured by a finer, porous system medium (plaster) over a coarser porous system. The presence of linseed oil in the limewash does not seem to affect the development of salt efflorescence in respect to the pure limewash, except in the case of the limewash with 3% of oil, which showed mass values of salt efflorescence similar to the uncoated specimens.

The Opuka stone reference (uncoated) developed a much smaller amount of salt efflorescence in respect to Mšené. In the case of the painted specimens, most of the salt

developed between the paint layer and beneath the stone's surface, as mentioned. These results are further discussed with the images taken under SEM. The amount of debris was greater in the limewashed specimens but this also included the paint layer which was completely detached from the stone in all cases. The severity of damage seemed to increase with increasing oil dosage in the limewash, probably by making the salt solution front recede deeper in the subsurface during Stage II drying, which is dominated by water vapour diffusion.

The SEM photographs and EDX elemental maps of the cross-sections of Mšené and Opuka stone are shown in Figures 8 and 9, respectively. In Mšené stone, it is possible to observe that the limewashes penetrated up to 100 μm deep in the stone (Figure 8c,d), which is in line with the lime particle size and the stone pore size mentioned earlier. The four paint coats are clearly distinguishable by a dense thin layer between each coat, probably formed during drying in between each application by migration of the finest particles to the surface. The thickness of the paint layers decreases from the first to the last, in line with the limewash consumption (Figure 1a); this is probably due to the effect of pore filling in the first coats. The contact zone between the lime and the stone grains is generally good, though some voids can be observed at some points. No significant differences were observed between the pure limewash and the limewash with linseed oil. These observations support the previously mentioned findings of more effective moisture and salt transport in limewashed Mšené stone.

The structure of the paint layers in Opuka is completely different from that observed in Mšené (Figure 9). In this case, the four paint coats are virtually indistinguishable, and the total thickness of the coat is smaller. This is also in line with the amount of limewash uptake (Figure 1b), lime particle size, and stone pore size. The most striking feature is that the coat did not adhere to the stone surface, i.e., there is no contact between the lime particles and the stone matrix. This explains why the paint layer easily detached from the surface during drying with the NaCl solution. Consolidation trials with nanolime suspensions (CaLoSil IP25) in Opuka stone revealed that the product did not penetrate the pores and remained at the surface due to the very low pore size of the stone [31].

4. Conclusions

Limewash is a material that is generally physically and chemically compatible with the most traditional porous building materials such as stone, brick, lime-based mortars, earthen substrates.

Limewash with linseed oil forms a protective coating that allows the drying of the underlying substrate. However, it can supress the transit of salt; this is dependent both on the level of water-repellence and on the porous network of the substrate. The following main conclusions can be drawn from the present study:

- Increasing the oil dosage induces an increment in the degree of water-repellence of the limewash in both stones, though none achieved hydrophobic properties; this increment is more or less linear with increasing amount of oil added.
- There is a substantial reduction of the capillarity water absorption rate in Mšené coated with limewashes. Pure limewash alone promoted a relevant decrease in the capillary water uptake, further enhanced with increasing oil dosage. In the case of Opuka, the water absorption rate is considerably less influenced by the limewashes compared with Mšené.
- The effect of the limewashes on the drying with pure water was not very significant with both pure limewash and limewash with linseed oil. The drying rate was slightly accelerated by the pure limewash, which is in line with other studies.
- The evaporation rate was substantially reduced in the presence of the NaCl solution in comparison with that of pure water. Only salt efflorescence developed in Mšené and the limewash seemed to favour the development of efflorescence without damaging the paint, whereas bulging of the paint and delamination of the stone surface occurred in all Opuka specimens.

- In Mšené stone, lime can penetrate into the pores of the stone matrix and favour moisture and salt transport. In the case of Opuka, lime remains at the surface and shows no adhesion to the substrate.

The results obtained show that the type of limewash used in this study is not effective for the protection of substrates with very low pore size such as Opuka, but further tests also taking into account the roughness of the surface and the chemical affinity should be undertaken. The use of lime putty with smaller particle size and the preparation of suspensions with a lower concentration of calcium hydroxide should be considered to overcome the low adhesion of the limewash to Opuka stone. In the case of substrates with a wider pore size distribution, such as Mšené stone, the limewashes prepared in this study show promising compatibility results, so they can be effective in the protection against water ingress in damp and salt-contaminated substrates. Future work should consider durability tests using larger specimens and onsite trials on old and new constructions.

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