

Article

# The Influence of 30 Years Outdoor Weathering on the Durability of Hydrophobic Agents Applied on Obernkirchener Sandstones

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**Abstract:** The durability of eleven different water repellents applied on one sandstone type was studied after a long-term weathering at seven different locations in Germany. By measuring colour changes, it could be shown that the formation of black crusts, the deposition of particles and biogenic growth caused a gradual darkening as well as significant changes in total colour over time. Additionally, the water absorption behaviour was investigated with two different methods: applying a low pressure using the pipe method and capillary water absorption measurements from a wet underlay. Afterwards, the test results were analysed with four different evaluation methods: calculation of the protection degree from pipe method and capillary water absorption, determination of the velocity of water uptake during capillary water absorption and calculation of the damaged depth of the stone surface using single-sided NMR technique. The growing damaged depth leads to an increase of the water uptake velocity and to a decrease of the protection degree of the applied hydrophobing agents. Three protective agents based on isobutyltrimethoxysilane showed already after two years of outdoor weathering a clear loss of performance, which significantly increased after 30 years of exposure.

**Keywords:** conservation; natural stone; long-term weathered; water repellents; durability; single-sided NMR

## 1. Introduction

Most of our historical stone buildings and monuments are made of sedimentary rocks. Their mineral composition and physical structure, in combination with varying pore space characteristics, limit their durability in terms of weathering influences. In order to reduce the susceptibility to weathering, water repellents based on organosilicon compounds can be used. The long-term impact of these stone treatments is a controversial issue [1–3]: on the one hand, the capillary water ingress is significantly reduced, which prevents stone deterioration processes based on the influence of water. On the other hand, the possible decrease of water vapour diffusion through the pore system can lead to hygric expansion inside the stone, which causes in combination with freeze-thaw cycles spalling of the treated stone area. Furthermore, the long-term behaviour and efficiency of these stone treatments depends on diverse aspects and is still a scientific issue [4–7]. The type of stone (e.g., sandstone, limestone, igneous or metamorphic rocks) as well as the chemical composition of the used conservative (e.g., acrylic polymers or organosilicon compounds) and also its application have a significant influence on the success of a conservation action, e.g., an incorrect performance or a poor adhesion of the water repellent with the stone substrate can lead to severe damage over time [8–10].

Finding answers concerning the above-mentioned issues, the Zollern-Institute (Deutsches Bergbau Museum, Bochum) performed between 1986 and 2017 a field study in Germany, where various types

of natural stones were exposed to different weathering conditions. In addition, reference samples were also deposited in an archive over the entire period. For each type of stone and each location, 11 specimens were applied with different hydrophobing agents based on organosilicon compounds, while 2 specimens stayed untreated [11,12].

This study focuses on the evaluation of these long-term weathered samples treated with 11 different water repellents, as shown on one sandstone type. The aim of this research is the performance analysis of the applied hydrophobic agents. The influence of the composition of the agents, leading among other things to various penetration depths, is determined with three different test methods. Based on the work done in [13], a damaged depth inside the weathered stone is calculated for the first time. The term damaged depth describes the extent of damage in the uppermost area of the natural stone surface. A comparison between damaged depth of the stone surfaces and penetration depth of the agents allows statements concerning the performance and explains partly unsolved results concerning the here evaluated protection degrees.

## 2. Experimental Matrix

Investigations were carried out on a frequently used building stone in Germany, namely the Obernkirchener Sandstone (OKS). The mineral composition as well as the geotechnical properties of this sandstone type are listed in Table 1.

**Table 1.** Petrographic and petrophysical properties of Obernkirchener Sandstone.

Stone Type	Obernkirchener Sandstone OKS
colour	beige to yellowish-grey, 5 Y 8/1–5 Y 7/2
mineral content [14]	quartz 81%, rock fragments 17%, muscovite (subordinated)
matrix	quartzitic, kaolinitic
classification	fine-grained quartzitic sandstone
total porosity [%]	20
bulk density [g/cm <sup>3</sup> ]	2.16
apparent density [g/cm <sup>3</sup> ]	2.71
average pore radius [µm]	3.4

The samples have a triangle-prismatic-shaped structure with a length of 300 mm. Figure 1 shows the geometry of the samples as well as the further preparation for the investigations. To assess the weathering effects and the degradation of the hydrophobic agents on a time-related basis, specimens were taken from these stone samples after an exposure time of 2, 24 or 30 years. At each time step, a 30 mm thick slice was cut out from the lateral surfaces (marked green) of each sample (Figure 1). All investigations described in this study were carried out on these segments at the TU Dortmund. The triangle-shaped slices, which were cut out after 2 years of natural weathering, were stored in an archive until the examinations were carried out in the years 2018 and 2019.

In 1986, the dry samples were applied with 11 different water repellents based on organosilicon compounds. In order to generate a uniformly wetted surface everywhere, the samples were completely immersed in a container filled with the respective hydrophobic agents and treated by flood-process with an application time of one minute. Table 2 provides an overview of the chemical composition and active ingredient content of the used products as well as characteristic values of OKS treated with these agents. The penetration depth of the hydrophobic agents was measured with a calliper on the triangle-shaped slices, which were moistened for this purpose [1,2,13]. The measurement was carried out on the cut side. The mean values and the standard deviations in Table 2 were calculated in each case from 42 measuring points.



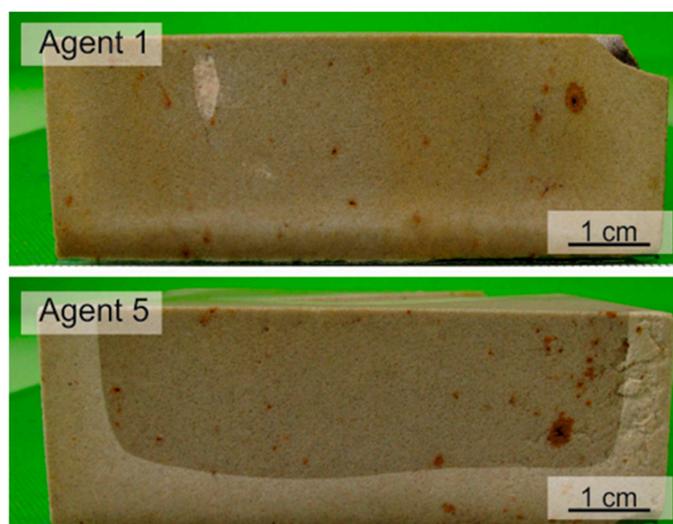
**Figure 1.** Left: The geometry of the samples and the sampling of the sample slices after 2 and 30 years, here marked green (years = a). Right: Outdoor weathering of the samples in Nuremberg after an exposure time of 30 years.

**Table 2.** Overview of the applied protective agents and characteristic values of Obernkirchener Sandstone treated with these agents ( $\pm$ standard deviation).

No.	Protective Agent and Content [M.-%]	Penetration Depth [mm]	Water Absorption after 1 h [ $\text{kg}/\text{m}^2$ ]	Increase of Water Vapour Diffusion Resistance Value [%]
0	untreated Obernkirchener Sandstone, 2a indoor (reference)	-	1.38	
1	34% propyl-/ 5% octyltrimethoxysilane	$7.0 \pm 1.8$	0.03	16
2	35% isobutyltrimethoxysilane	$3.3 \pm 3.1$	0.04	5
3	20% isobutyltrimethoxysilane + 20% tetraethoxysilanehydrolysate	$3.3 \pm 2.1$	0.03	15
4	20% isobutyltrimethoxysilane + 20% tetraethoxysilane	$2.6 \pm 2.5$	0.04	12
5	low-molecular methylethoxysiloxane + tetraethoxysilane ( $\Sigma 75\%$ )	$6.7 \pm 1.5$	0.03	11
6	7.5% low-molecular methylethoxysiloxane	$4.0 \pm 0.6$	0.02	18
7	6.7% oligomer methylethoxysiloxane	$3.3 \pm 0.5$	0.03	17
8	5% methyl-/isooctyl silicone resin	$3.4 \pm 1.4$		14
9	6.7% oligomer methyl-/isooctylmethoxysiloxane	$2.9 \pm 1.1$	0.03	13
10	oligomer methyl-/isooctylmethoxy-siloxane + tetraethoxysilane ( $\Sigma 8.3\%$ )	$3.6 \pm 0.8$	0.03	8
11	8% polymeric methylmethoxy-siloxane (silicone resin)	$3.4 \pm 0.6$	0.03	17

The hydrophobic agents with the identification numbers 1, 2, 3 and 4 are based on silane whereby agents 1 and 2 include the highest silane contents and agents 3 and 4 additionally contain silicic acid ester (tetraethoxysilane). The impregnation depth of the water repellents containing isobutyltrimethoxysilane (agents 2, 3 and 4) is more than twice lower compared to agent 1 and has a high standard deviation. These high standard deviations suggest that the hydrophobic agents, based on silane, penetrate uneven into the pore system of the sandstones. Furthermore, these materials showed no clear line between hydrophilic and hydrophobic zone [13]. The other materials, especially based on siloxane, showed after wetting the surface a clear boundary between dry (hydrophobic) and wet (hydrophilic). Figure 2 visualizes exemplary two samples with high penetration depth and compares the boundaries of agent No. 1 and 5. Agents 5, 6, 7, 9 and 10 are based on siloxane and allow

the comparison of low-molecular and oligomer methylethoxysiloxane as well as methylethoxy- and methyl-/isooctylmethoxysiloxane. The third group is based on silicone resin (agents 8 and 11).



**Figure 2.** Visual penetration depth of agent No. and 5 after wetting the samples.

The capillary water absorption measured according to DIN EN 15801 [15] demonstrates the effectiveness of all hydrophobing agents applied on OKS. The increase in water vapour diffusion resistance was determined in relation to the untreated samples. For this reference value, the water vapour diffusion resistance of the two untreated samples was averaged from each location (mean value of 24 samples and standard deviation:  $37.8 \pm 4$ ). The values were measured by wet cup test according to DIN EN 15803 [16,17]. Due to application of the hydrophobic agents, the water vapour diffusion resistance increased up to 18% but stayed still under the threshold value of 50% required by [2]. Obviously, the addition of silicic acid ester has no influence on the water vapour diffusion resistance.

All samples of the triangle-prismatic-shaped Obernkirchener Sandstones were exposed at seven different locations in Germany in 1986/1987. Three locations were situated in North Rhine-Westphalia, Dortmund, Duisburg and Eifel, and three in Bavaria, Nuremberg, Munich and Kempten. Table 3 lists a detailed description of the exposure sites and their surrounding environments. The seventh site was indoor and can be used as reference.

**Table 3.** Description of the exposure sites and their setting.

Location	Exposure Site	Setting
Dortmund	located in the west of the city, on an old colliery site (former heavy industrial site) with traffic around, exposure stations situated under trees	residential area/industrial area
Duisburg	located in the north of the city, exposure stations situated on the green area of a schoolyard under trees	residential area/heavy industrial area
Eifel	located on agricultural land, exposure stations situated on the edge of a forest	urban area and rural space in the countryside
Nuremberg	located in the north-west of the city, near a water treatment plant, on a busy street behind bushes	urban area
Munich	located in the south-west of downtown with a high amount of traffic around the site, exposure stations situated partly under trees	residential area/business area
Kempten	exposure stations situated on the roof of a tree nursery	residential area

For the above-stated weathering locations, their mean climatic data is shown in Table 4. These are averages of the last 10 years of exposure (Dortmund, Duisburg, Eifel: 2000–2009; Nuremberg, Munich, Kempten: 2007–2016) from measuring stations near the locations and with similar environmental conditions. An extensive evaluation of the climatic data for temperature, relative humidity and precipitation on the basis of hourly values has been carried out, in order to obtain differentiated information with regard to the duration of certain temperature levels, the number of freeze-thaw changes, annual precipitation times and precipitation frequencies. In addition, the averaged pollutant values for nitrogen- and sulphur-dioxide are given for this period.

In the considered period, the temperatures below the freezing point were more present at the Bavarian locations, especially in Kempten. In addition, the number of hours with a relative humidity above 80% was higher for the locations Eifel and Kempten compared to the other sites. A high precipitation rate was recorded in Kempten, while it did not rain many times. The pollution data showed a low NO<sub>2</sub> rate in Eifel, whose exposure site is situated in an agricultural landscape, while in the urban location Munich the values are significant higher. Concerning SO<sub>2</sub>, the heavy industrial setting in Duisburg had the highest pollution rate.

**Table 4.** Climatic data for the weathering locations, mean values over the last 10 years of exposure (a = year, h = hours).

Title	Exposure Site above Mean Sea Level [m a.s.l.]	Temperature		Freeze- Thaw- Changes [1/a]	Relative Humidity		Precipitation		Pollution	
		<0 °C	>25 °C		<50%	>80%	[times/a]	[mm/a]	NO <sub>2</sub>	SO <sub>2</sub>
		[times in h/a]	[times in h/a]		[times in h/a]	[times in h/a]	[times/a]	[mm/a]	[µg/m <sup>3</sup> ]	[µg/m <sup>3</sup> ]
Dortmund	126	587	274	97	935	5014			30.4	5.7
Duisburg	18	441	352	83	1050	4775	527	947	31.1	11.1
Eifel	579	990	64	91	320	6129	521	820	9.2	5.4
Nuremberg	299	968	309	130	975	4753	447	631	28.2	x *
Munich	552	914	333	97	1126	3929	408	938	67.9	4.0
Kempten	661	1343	206	189	751	5166	381	1177	22.0	x *

Sources:  <https://www.lanuv.nrw.de/umwelt/luft/immissionen/messorte-und-werte>, \* no values available  
 [https://opendata.dwd.de/climate\\_environment/CDC/](https://opendata.dwd.de/climate_environment/CDC/); <https://www.umweltbundesamt.de/themen/luft/luftschadstoffe/stickstoffoxide>; <https://www.umweltbundesamt.de/themen/luft/luftschadstoffe/schwefeldioxid>.

### 3. Experimental Methods

#### 3.1. Optical Surface Changes and Colorimetry

Optical changes caused by the influence of outdoor weathering or by the conservation action itself were evaluated by colour measurements performed according to DIN EN 16851 [18] and DIN EN 15886 [19]. Measurements were carried out using the spectrophotometer spectro-guide sphere gloss from BYK-Gardner with a standardised light of D65, a 10° image field size and a measuring geometry of d/8°. The examinations were carried out on the triangle-shaped slices (Figure 1). On both the treated weathered side and the cut side (unweathered-untreated  $\hat{=}$  reference), 5 measuring points were determined, and the mean values and standard deviations were calculated. The results were presented in the CIE L\*a\*b\* colour system, where colour is expressed with the following parameters: L\* is the lightness (black (0) to white (100)), a\* the red (a\*)–green (-a\*) coordinate and b\* the yellow (b\*)–blue (-b\*) coordinate in a Cartesian coordinate system.

An ideal hydrophobing agent does not significantly influence the visual appearance of the natural stone surfaces, and despite of natural weathering processes, the treated surfaces should also be stain-repellent, which is why these coordinate values should not change noticeable over time. To evaluate variations in the optical appearance of the samples over time, with  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$ , the total colour difference  $\Delta E^*$  was calculated according to Equation (1):

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

A  $\Delta E^* > 5$  units is rated as a different colour and represents in this paper the limit value of noticeable changes (dashed lines in the diagrams) [20,21].

### 3.2. Measurement of Water Absorption by Pipe Method (Karsten Tube)

According to DIN EN 16302 [22] an open glass pipe was mounted with a fixing compound on the stone surface and the graded tube was filled with water. The amount of water absorbed over an area of 5.7 cm<sup>2</sup> has been determined in defined time steps up to one hour. The tests were carried out using a tube for horizontal surfaces. The water pressure of 10 mbar was kept constant during the measurements. The investigations were done on untreated and treated stones after 0, 2 and 24 or 30 years of natural weathering. Afterwards the protection degree PD<sub>LP</sub> was calculated with Equation (2) according to DIN EN 16581 [18]. While the standard just mentions that the value should be near 100% for a hydrophobic function, this paper proposes the following three classes:

- Protection degree 100% to 95%: hydrophobic;
- Protection degree 94% to 90%: influenced by a hydrophobic effect;
- Protection degree  $\leq 89\%$ : hydrophilic.

$$PD_{LP}(\%) = \frac{(W_f)_B - (W_f)_A}{(W_f)_B} \times 100 \quad (2)$$

with

PD<sub>LP</sub>—protection degree under low water pressure for 1 h; in%  
 (W<sub>f</sub>)<sub>B</sub>—absorbed amount of water of untreated sandstone after 2 years indoor storage in mL/cm<sup>2</sup>;  
 (W<sub>f</sub>)<sub>A</sub>—absorbed amount of water of treated sandstone in mL/cm<sup>2</sup>.

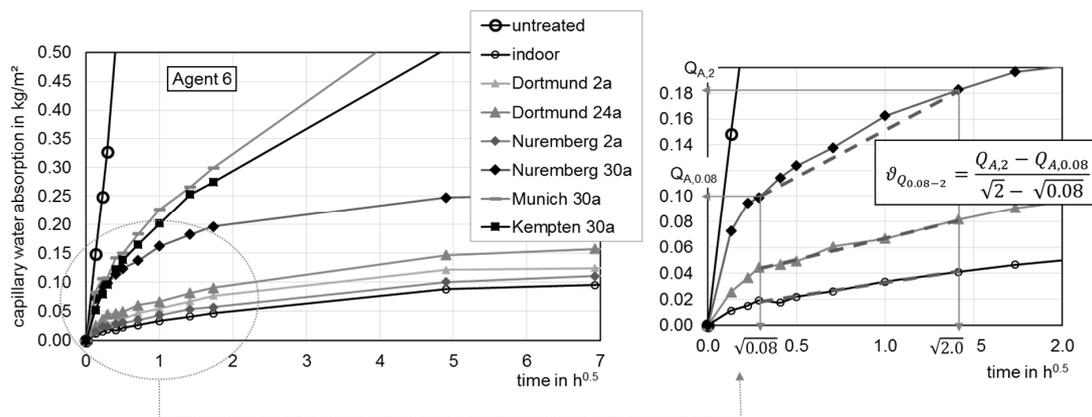
### 3.3. Measurement of Capillary Water Absorption

According to DIN EN 15801 [15] the capillary water absorption was determined by placing the samples with their weathered side on a wet underlay and measuring the weight changes after different time periods up to 72 h. The test was done on untreated and treated OKS after 2 and 24 or 30 years of natural weathering. Afterwards, the mass changes related to the contact area can be drawn in a diagram as function of the square root of time. Using the square root of time, nearly linear gradients for the amount of water uptake occur (compare [3,15,23]). As described in Figure 3 and Equation (3), the velocity of water uptake between 5 and 120 min was calculated.

$$\vartheta_{Q_{0.08-2}} = \frac{Q_{A,2} - Q_{A,0.08}}{\sqrt{2} - \sqrt{0.08}} \text{ in } \left[ \frac{\text{g}}{\text{m}^2 \cdot \sqrt{\text{h}}} \right]. \quad (3)$$

with

$\vartheta_{Q_{0.08-2}}$ —velocity of water uptake between  $\sqrt{0.08}$  and  $\sqrt{2}$  h in g/m<sup>2</sup>  $\sqrt{\text{h}}$ ;  
 Q<sub>A,2</sub>—absorbed amount of water after 2 h in g/m<sup>2</sup>;  
 Q<sub>A,0.08</sub>—absorbed amount of water after 0.08 h in g/m<sup>2</sup>.



**Figure 3.** Evaluation of the capillary water absorption with regard to the velocity of water uptake during a period of 5 to 120 min, exemplary shown for agent 6 (a = year).

Furthermore, the protection degree  $PD_{Ci}$  was calculated with Equation (4):

$$PD_{Ci}(\%) = \frac{(Q_{Bi} - Q_{Ai})}{Q_{Bi}} \times 100 \tag{4}$$

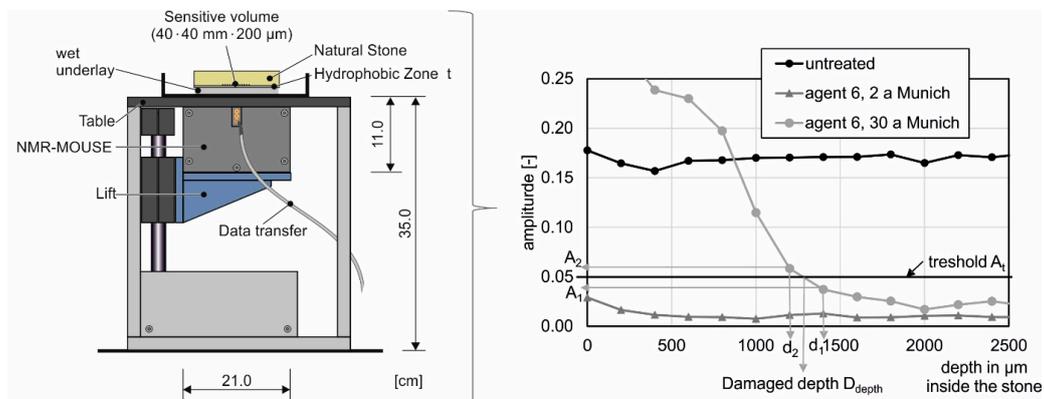
with

$Q_{Bi}$ —absorbed amount of water of untreated sandstone after 2 years indoor storage at the time  $t_i$ ;  
 $Q_{Ai}$ —absorbed amount of water of treated sandstone at the time  $t_i$ .

### 3.4. Moisture Distribution Inside the Stone—Degradation Depth

The NMR MOUSE<sup>®</sup> PM 25 (Mobile Universal Surface Explorer, registered trademark of RWTH Aachen University, Aachen, Germany) allows the non-destructive detection of moisture distribution inside porous materials via nuclear magnetic resonance. The measurement technique is described amongst others in [13,24,25].

In situ capillary water absorption tests were carried out on the top Table above the NMR sensor while the NMR measuring volume ( $40 \times 40 \times 0.2$  mm) was moved through the stone, beginning at the stone surface up to a final depth of 4.4 mm. Figure 4 shows the test set up and an exemplary measuring curve. The amplitude (signal of proton density) depends on the amount of water in the porous stone.



**Figure 4.** Test set up of in situ NMR measurements during capillary water absorption and determination of the depth of damage after 30 years of outdoor weathering in Munich, shown as an example with protective agent 6.

Based on 51 measurements, a correlation between amplitude and amount of absorbed water was determined for untreated and treated OKS [13]. A threshold for the amplitude was defined: if the amplitude is  $\leq 0.05$  the water content is  $\leq 0.1 \text{ kg/m}^2$  and the protection degree is  $\geq 95\%$ . According to the critical values mentioned in [2] and our own experience, this threshold allows the classification between hydrophobic or just an influenced zone. With this threshold and assuming a linear gradient of the amplitude between the two measuring points nearest to the threshold, the damaged depth can be calculated with Equation (5):

$$D_{\text{depth}} = \frac{(A_t - A_1) \cdot (d_2 - d_1)}{(A_2 - A_1)} + d_2 \quad (5)$$

with

$D_{\text{depth}}$ —damaged depth inside the natural stone in [ $\mu\text{m}$ ];

$A_t$ —threshold amplitude, for Obernkirchener Sandstone 0.05 in [-];

$A_1$ —measured amplitude directly below the threshold amplitude in [-];

$A_2$ —measured amplitude directly above the threshold amplitude in [-];

$d_1$ —corresponding depth in which amplitude  $A_1$  is measured in [ $\mu\text{m}$ ];

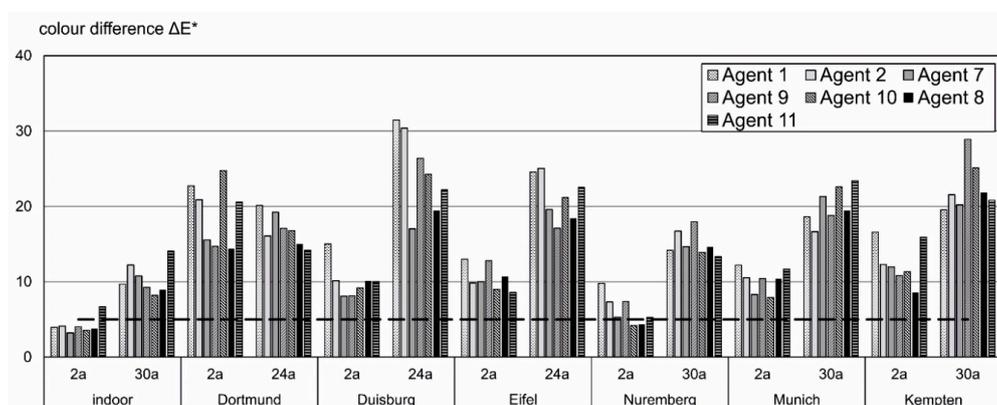
$d_2$ —corresponding depth in which amplitude  $A_2$  is measured in [ $\mu\text{m}$ ].

Based on water absorption measurements on treated OKS samples (Table 2) it could be shown that all applied hydrophobing agents are initially effective. As a result of a natural weathering time of 30 years, changes occur in the hydrophobized zone. This is caused by soiling, biogenic growth, a reduction of the water-repellent effect and loosening of the stone structure. These changes are associated with an increase in the amount of absorbed water in the uppermost area of the stone surface (Figure 4). With the determination of a limit value for the loss of hydrophobicity, this damaged depth can now be determined with Equation (5).

## 4. Results and Discussion

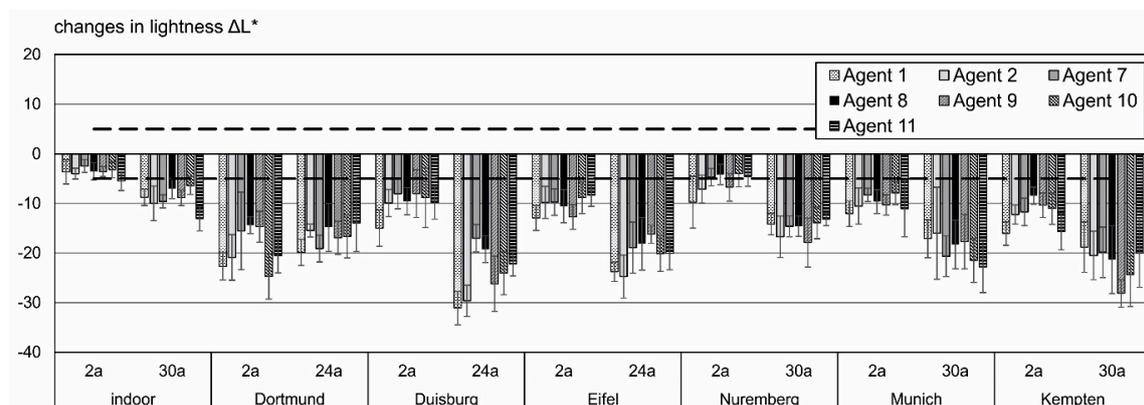
### 4.1. Optical Surface Changes and Colorimetry

Figure 5 presents the results of the total colour difference ( $\Delta E^*$ ) and changes in lightness ( $\Delta L^*$ ) for different treated OKS samples. It can be seen that the initial treatment (Figure 5, indoor 2a) did not cause significant changes of  $\Delta E^*$  as the values are below the limit value of 5 (except agent 11). However, due to the application of these different hydrophobing agents the surface darkens, leading from the beginning on to optical aesthetic changes of the stone surfaces (see Figure 6, indoor 2a). After a storage time of 30 years (indoor 30a), the surface discoloured, probably because of the dusty environment in the archive.



**Figure 5.** Total colour difference  $\Delta E^*$  of Obernkirchener Sandstone (OKS) samples, treated with silanes (agent 1, 2), siloxanes (agent 7, 9, 10) and silicone resins (agent 8, 11) from different exposition sites.

Except for treated OKS samples exposed in Dortmund,  $\Delta E^*$  and  $\Delta L^*$  increased after 24 years of outdoor exposure on all exposition sites by a factor of 2. A maximum  $\Delta E^*$  has been measured on silane treated samples, which were exposed for 24 years in Duisburg (agent 1 = 31; agent 2 = 30). On the exposition sites in North Rhine-Westphalia, the colour differences and differences in  $\Delta L^*$  are higher for samples impregnated with silane-based products than for siloxane or silicone resin impregnated stone surfaces. In contrast,  $\Delta E^*$  increased for siloxane treated samples from the locations in southern Germany. In addition, these samples show a significant darkening over time (Figure 6).



**Figure 6.**  $\Delta L^*$  values of OKS samples, treated with silanes (agent 1, 2), siloxanes (agent 7, 9, 10) and silicone resins (agent 8, 11) from different exposition sites.

Slight changes in total colour and lightness could be detected for the treated samples exposed in Dortmund, where no distinct variations appeared during a time period of 24 years. The visible and measured colour changes are caused by biological growth, the deposition of particles and the formation of black crusts on the OKS surfaces, which lead to a gradual darkening as well as a significant change of the optical appearance (compare also with [26,27]).

#### 4.2. Comparison of the Protection Degree Calculated from Water Absorption by Pipe Method and Capillary Water Absorption

Table 5 summarises the protection degree  $PD_{LP}$  calculated from water absorption measurements by pipe method after 1 h (Equation (2)) for the 11 protective agents applied on OKS. In general, the hydrophobic surfaces withstand a water pressure of 10 mbar for one hour after a long-term weathering at the different outdoor locations. After 24 as well as 30 years of outdoor weathering, only protective agent 9 (6.7% oligomer methyl-/isooctylmethoxysiloxane) has a consistent loss of its hydrophobic effect. After 2 years of outdoor weathering, the silane-based agents 2, 3 and 4 show partly a reduction in performance. The increase in the water-repellent effect after 30 years compared to 2 years of outdoor weathering with agents 2, 3 and 4 seems somewhat surprising. Two different reasons could cause this effect: (a) the influence of biogenic growth and (b) the very uneven penetration of the isobutyltrimethoxysilanes into the stone. The following results (Table 6 and Figures 7 and 8) show that these agents are no longer effective even after 30 years.

Table 6 summarises the protection degree  $PD_{Ci}$  calculated from capillary water absorption tests after 1 h measuring time (Equation (4)) for the 11 protective agents applied on OKS after outdoor weathering. In contrast to Table 5, all protective agents show after a long-term outdoor weathering a loss of effectiveness. Especially at the southern locations in Germany, a decrease of the hydrophobic effect can be seen on the treated samples after an exposure time of 30 years. The silane-based agents 2, 3 and 4 show already after 2 years of outdoor weathering a performance loss.

Comparing Tables 5 and 6, it is obvious that the two unequal measuring methods lead to different results concerning the performance of hydrophobic agents. This fact is well known in literature (compare for example [28]). To sum up, the application of 10 mbar water pressure does not affect the

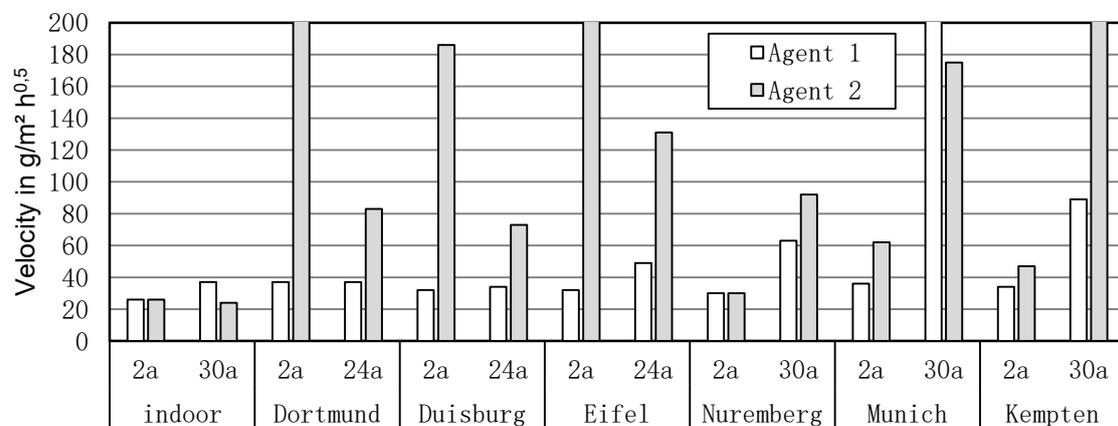
hydrophobic function while a superficial water contact with the total area of the treated stone with the wet underlay leads after more than 24 years outdoor weathering to a loss of the hydrophobic effect for all protective agents. A further evaluation of the capillary water absorption for a more detailed discussion concerning the effectiveness of the different protective agents is necessary.

**Table 5.** Protection degree  $PD_{LP}$  calculated from water absorption by pipe method after a weathering time of 2, 24 and 30 years, respectively, at the 7 locations (PD classes: 100% to 95%: hydrophobic (white cell), 94% to 90%: influenced by a hydrophobic effect (light grey cell),  $\leq 89\%$ : hydrophilic (grey cell)).

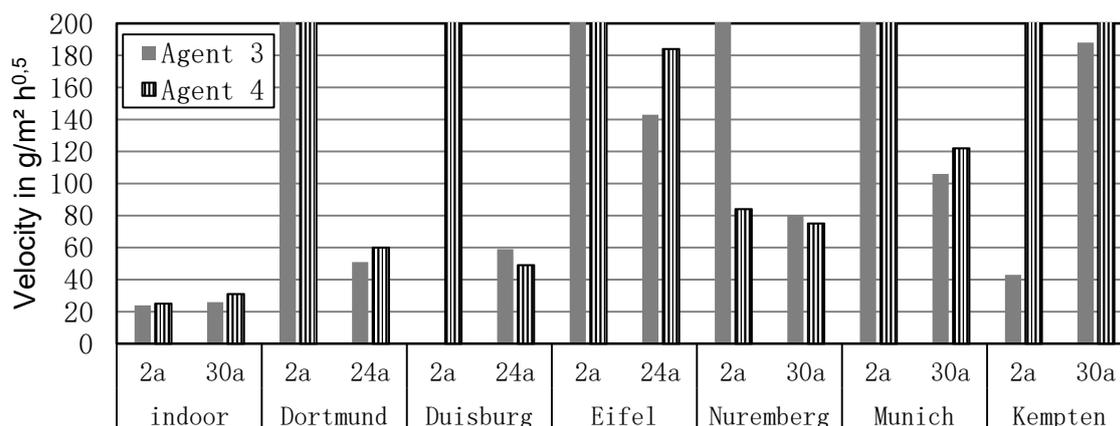
Agent	Indoor		Dortmund		Duisburg		Eifel		Nuremberg		Munich		Kempten	
	2a	30a	2a	24a	2a	24a	2a	24a	2a	30a	2a	30a	2a	30a
1	100	100	100	95	98	100	98	96	100	97	100	92	98	97
2	100	100	80	91	91	97	50	99	100	95	100	95	100	91
3	99	99	89	95	100	96	57	96	78	95	55	96	100	95
4	100	100	64	95	23	96	86	95	100	96	95	96	100	95
5	97	100	95	99	98	98	98	97	99	95	100	96	100	95
6	99	100	100	100	95	97	100	96	99	98	100	96	100	95
7	100	100	95	95	100	96	100	95	100	95	100	96	100	91
8	96	100	100	97	100	96	100	98	100	96	100	92	100	95
9	100	100	100	91	100	91	100	95	100	92	100	95	99	91
10	98	100	95	98	100	96	100	95	100	93	99	95	100	94
11	100	100	95	96	100	96	100	95	100	95	100	96	100	96

**Table 6.** Protection degree  $PD_{CI}$  calculated from capillary water absorption tests after a weathering time of 2, 24 and 30 years, respectively, at the 7 locations (PD classes: 100% to 95%: hydrophobic (white cell), 94% to 90%: influenced by a hydrophobic effect (light grey cell),  $\leq 89\%$ : hydrophilic (grey cell)).

Agent	Indoor		Dortmund		Duisburg		Eifel		Nuremberg		Munich		Kempten	
	2a	30a	2a	24a	2a	24a	2a	24a	2a	30a	2a	30a	2a	30a
1	98	97	95	93	95	88	94	86	96	90	95	81	96	87
2	97	98	85	88	85	81	42	81	95	85	93	80	95	76
3	98	97	82	88	90	66	89	69	87	71	85	95	81	81
4	97	96	65	90	83	91	76	87	93	89	87	85	83	80
5	97	96	95	90	93	92	95	91	95	89	95	87	95	87
6	98	98	96	95	97	88	95	92	97	89	96	84	96	85
7	98	97	95	86	97	92	96	89	97	84	95	83	95	79
8	98	97	96	93	97	93	97	92	98	88	95	81	96	87
9	98	97	94	89	97	86	95	85	96	83	95	78	96	82
10	97	98	90	90	95	90	96	90	96	87	95	84	96	83
11	98	97	96	94	97	93	96	90	97	90	96	88	96	87



**Figure 7.** Velocity of water uptake between 5 and 120 min for OKS samples treated with agents 1 and 2 and weathered at the 7 different locations.

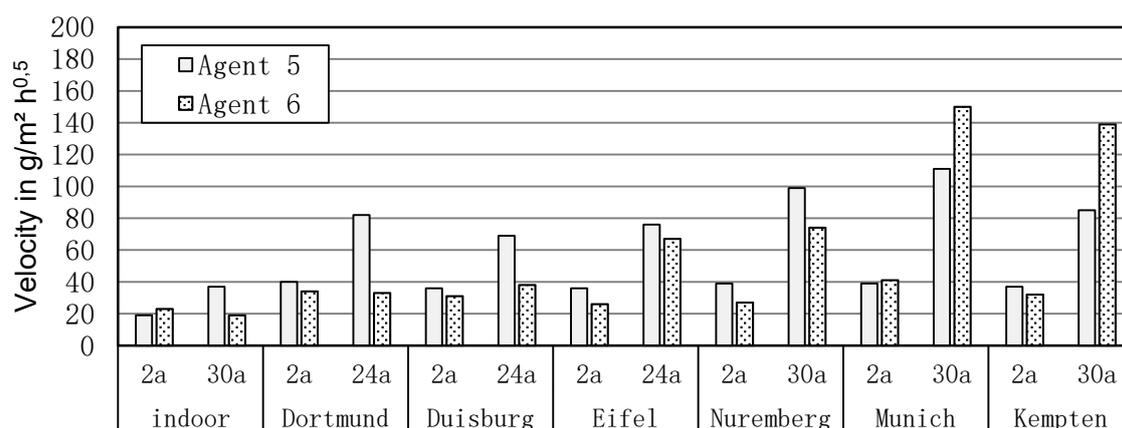


**Figure 8.** Velocity of water uptake between 5 and 120 min for OKS samples treated with agents 3 and 4 and weathered at the 7 different locations.

#### 4.3. Evaluation of the Protective Agents by the Velocity of Water Uptake

The velocity of water uptake between 5 and 120 min during the capillary absorption test was calculated with 3. While the untreated OKS has a velocity of water uptake  $\vartheta_{Q0.08-2}$  of nearly  $1400 \text{ g/m}^2 \text{ h}^{0.5}$ , the treated samples stored indoor have a value of about  $25 \text{ g/m}^2 \text{ h}^{0.5}$ . Figure 7 shows the differences in water uptake velocities of agent 1 and 2 applied on OKS. After 2 years of natural weathering of OKS samples treated with agent 1, the rate of water uptake increased only negligibly from  $26 \text{ g/m}^2 \text{ h}^{0.5}$  (indoor) to maximum  $37 \text{ g/m}^2 \text{ h}^{0.5}$  (Dortmund). The extension of the weathering time to 30 years led, at Nuremberg, Munich and Kempten, to more than a doubling of  $\vartheta_{Q0.08-2}$ . The highest value was calculated for Munich with  $214 \text{ g/m}^2 \text{ h}^{0.5}$ . In contrast, the OKS samples treated with agent 2 showed already after 2 years of exposure more than a doubling of  $\vartheta_{Q0.08-2}$  (except Nuremberg and Kempten). After 24 or 30 years, the values reached 73 to  $238 \text{ g/m}^2 \text{ h}^{0.5}$  (Kempten). These results explain the low protection degree  $PD_{Ci}$  of agent 2 (Table 6). An obvious reason for the insufficient effectiveness of agent 2 (35% isobutyltrimethoxysilane) is the uneven distribution of the agent inside the stone matrix of OKS, which varies between 0.8 and 8.3 mm. This irregular distribution was determined for all agents with isobutyl-structures. As a consequence, the velocity of water uptake also increased significantly for OKS samples treated with agents 3 and 4, already after a weathering time of 2 years. Due to the lower ingredient content of 20% isobutyltrimethoxysilane, the effectiveness of these agents is less pronounced than for agent 2 (Figure 8). The decrease of the velocity of water uptake after 24 years weathering especially in Dortmund and Duisburg compared to 2 years could be caused due to the uneven distribution of the agent inside the stone matrix and/or the bionic growth on the stone surface.

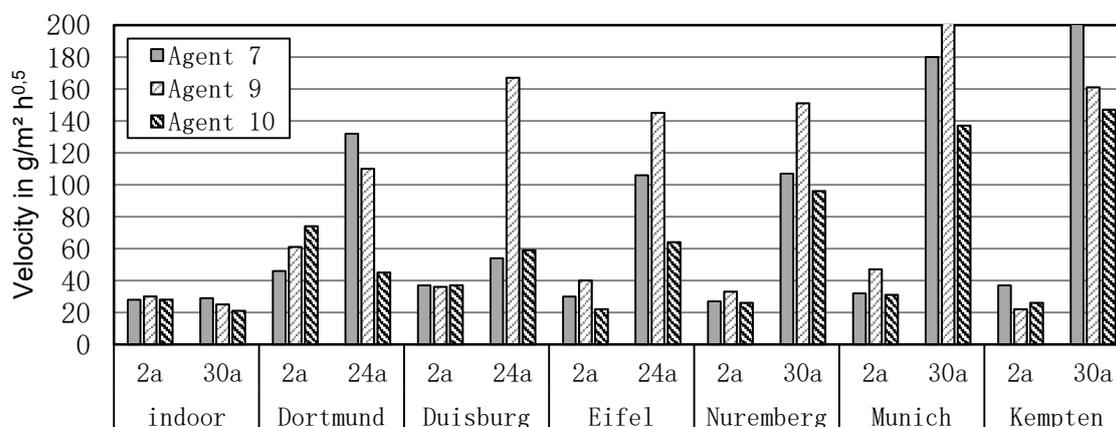
Figure 9 shows the velocity of water uptake for OKS samples treated with agents 5 and 6. The methylethoxysiloxane-agents are more effective than the silanes. The results show an increase in the velocity of water absorption after 24 years. This effect is more pronounced at locations in southern Germany.



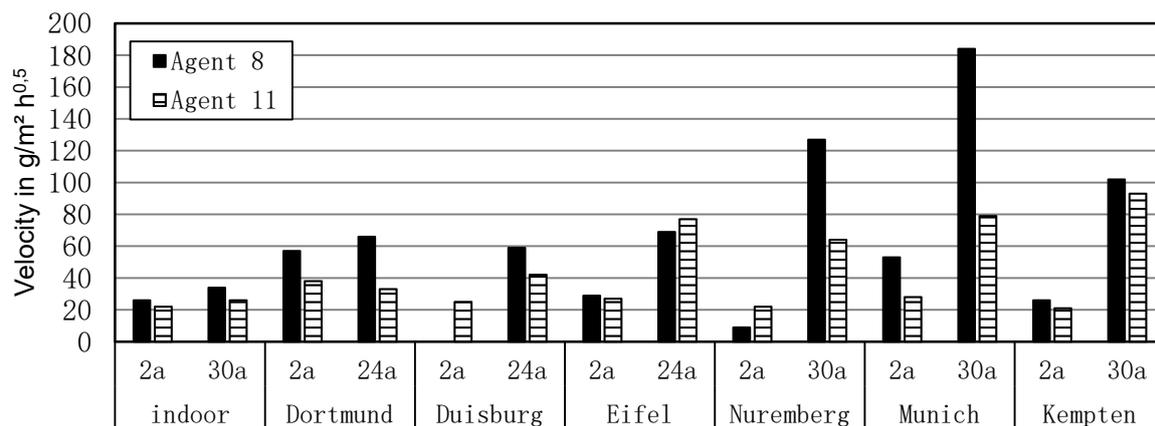
**Figure 9.** Velocity of water uptake between 5 and 120 min for OKS samples treated with agents 5 and 6 and weathered at the 7 different locations.

A comparison of the water uptake velocities of OKS samples treated with agents 7, 9 and 10 is shown in Figure 10. Two years of weathering at the different locations does not significantly influence  $\vartheta_{Q0.08-2}$  compared to the reference (2a indoor). After 24 and 30 years, respectively, outdoor weathering the OKS samples treated with agent 9 shows the highest increase of  $\vartheta_{Q0.08-2}$  up to 249 g/m<sup>2</sup> h<sup>0.5</sup> in Munich. At that time at each location, a loss of functionality can be stated for agent 9, which fits to the results shown in Tables 5 and 6. In contrast, the OKS samples treated with agent 7 show, after 24 years natural weathering in Duisburg, a lower increase of  $\vartheta_{Q0.08-2}$ . Agents 7 and 9 have the same oligomer siloxane content of 6.7%, but agent 9 has a methyl-/isooctylmethoxy-structure while agent 7 consist just of a methylethoxy-structure. The addition of tetraethoxysilane to the oligomer siloxane with methyl-/isooctylmethoxy-structure (agent 10) does not noticeably influence the results of  $\vartheta_{Q0.08-2}$ .

Figure 11 shows the velocity of water uptake for OKS samples treated with silicone resin. The lower agent content and/or the methyl-/isooctyl-structure of agent 8, compared to agent 11, which contains a methylmethoxy-structure (Table 2), leads to a higher water uptake rate after a long-term outdoor weathering. Again, the sample exposition at the southern locations of Germany led, after 30 years, to a significant increase of  $\vartheta_{Q0.08-2}$ . Samples from the rural region Eifel show, also after 24 years outdoor weathering, a clearer increase of  $\vartheta_{Q0.08-2}$  compared to samples exposed to the city regions Dortmund and Duisburg.



**Figure 10.** Velocity of water uptake between 5 and 120 min for OKS treated with agents 7, 9 and 10 and weathered at the 7 different locations.



**Figure 11.** Velocity of water uptake between 5 and 120 min for OKS treated with agent 8 and 11 and weathered at the 7 different locations.

#### 4.4. Evaluation of the Protective Agents by the Degradation Depth

Due to the non-destructive single-sided NMR technique described in Section 3.4, it is possible to detect indirectly the depth of damage (insufficient effectiveness) inside the treated Obernkirchener Sandstone. In Figure 12, the calculated damaged depth inside the OKS (Equation (5)) is compared with the measured penetration depth of the hydrophobic agents (measured visually with a calliper by wetting a cut edge). The high variation of the penetration depth of agent 2 is obvious. At the Eifel location, the damaged depth is higher than the penetration depth, which with 0.14 mm has the lowest value. The samples treated with agent 2 show a higher damaged depth compared to the samples treated with agent 1, which corresponds to the results discussed before (Figure 7).

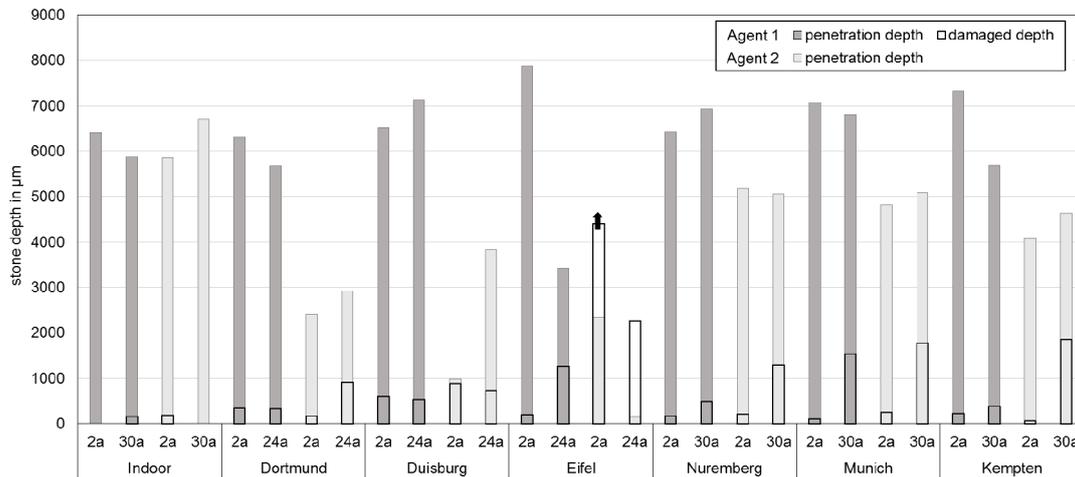
Figure 13 compares the penetration depth of agents 3 and 4 with their damaged depths. The acquisition of the damaged depths with the NMR technique is only possible to a depth of 4400  $\mu\text{m}$ . If the damaged depth reaches this value, it is marked with an arrow (Duisburg, Eifel, Munich). If the depth of damage exceeds the penetration depth, the speed of water absorption is over  $180 \text{ g/m}^2 \text{ h}^{0.5}$  (Figure 8), and the protection degree  $\text{PD}_{\text{Ci}}$  calculated from capillary water absorption is insufficient (Table 6). Once again, the depth of damage of these agents is often higher after 2 years than after 24 or 30 years, which in addition to the scattering of the penetration depth, suggests a reduction in water absorption due to pollution and bionic growth. This behaviour leads to the assumption that after an early damage of the hydrophobicity within 2 years, a stronger or different increase of bionic growth and pollution causes a compaction of the stone surface in such a way that the water absorption is reduced. This assumption will be considered in further investigations.

Figure 14 confirms the functionality of agents 5 and 6 even after 30 years of outdoor weathering. The depth of damage reaches a maximum of 1280  $\mu\text{m}$  in Munich. Similar results were determined for agents 8 and 11 (Figure 15). In general, the damaged depth increases with increasing weathering time.

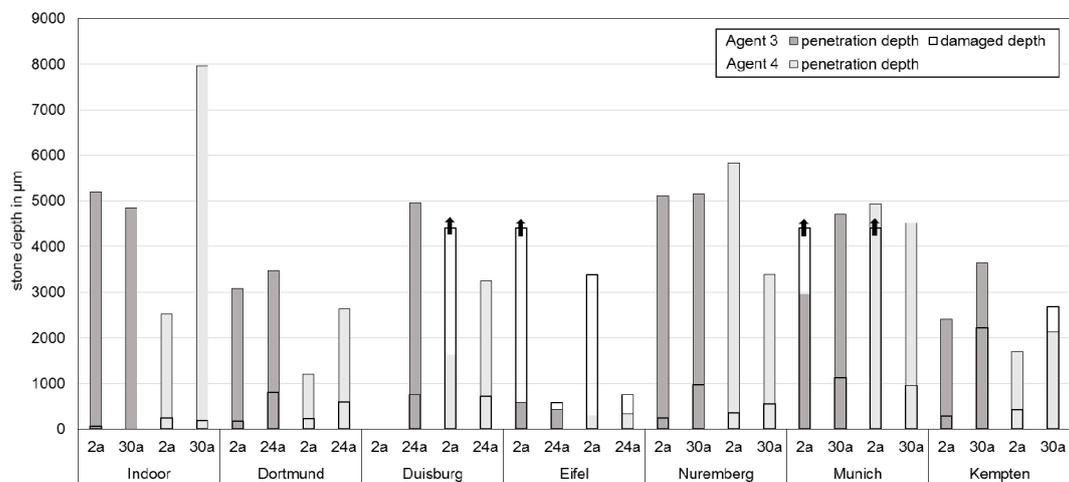
Figure 16 compares the penetration depths of agents 7, 9 and 10 with their damaged depths. Again, the damaged depth increased after 24 or 30 years of outdoor weathering, especially for samples exposed to the southern locations, which are characterised by a longer weathering time and a rougher climate. Agents 7 and 9 tend to show a higher depth of damage after 24 or 30 years, respectively, compared to agent 10.

For OKS samples treated with agents 1, 5, 6, 8, 10 and 11, a maximum damaged depth of about 1.5 mm was found, which is in general more than a third lower than the penetration depth. These results explain the increase of capillary water uptake which resulted in a decrease of the protection degree  $\text{PD}_{\text{Ci}}$  and an increase of the rate of water uptake during the first 120 min measuring time. This fact might also explain the slight changes of the protection degree  $\text{PD}_{\text{LP}}$ . The performance of the hydrophobing agents in deeper stone depths prevent the ingress of water under low pressure.

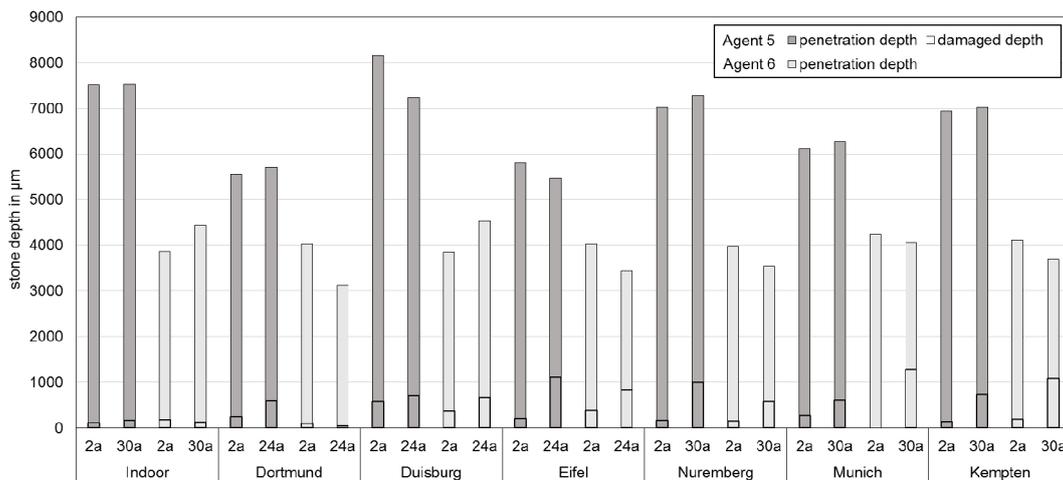
A correlation between the determined damaged depth and the penetration depth of the hydrophobic agents could not be established from the data. This result can be stated for all samples treated with the different agents. This indicates that a high penetration depth of the active substance does not necessarily mean that the durability of the treatment is increased. If the damaged depth reaches nearly the penetration depth, a loss of performance can be found for all investigated samples, for example, agent 9 after 30 years in Kempten.



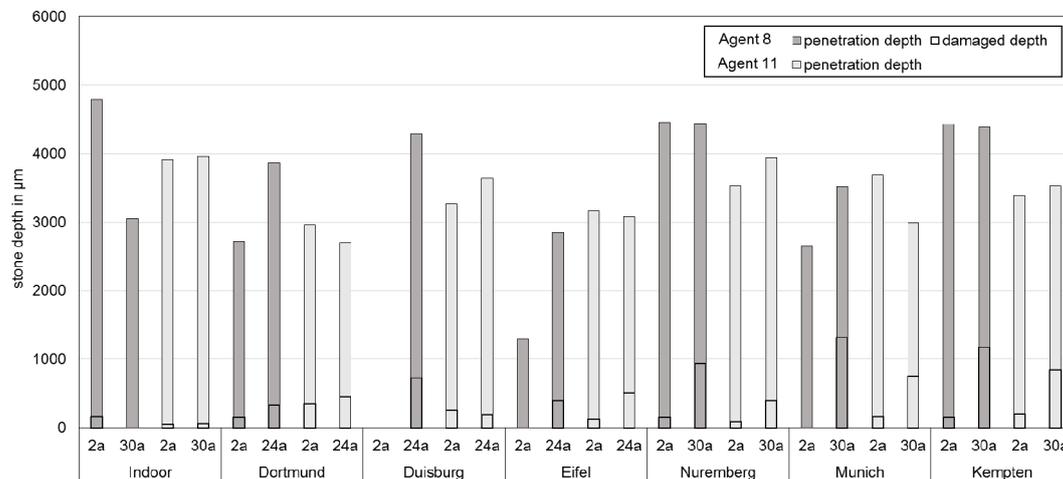
**Figure 12.** Comparison of the penetration depth of agents 1 or 2 applied on OKS with the damaged depth calculated with Equation (5) (depth 0 = surface of the stone).



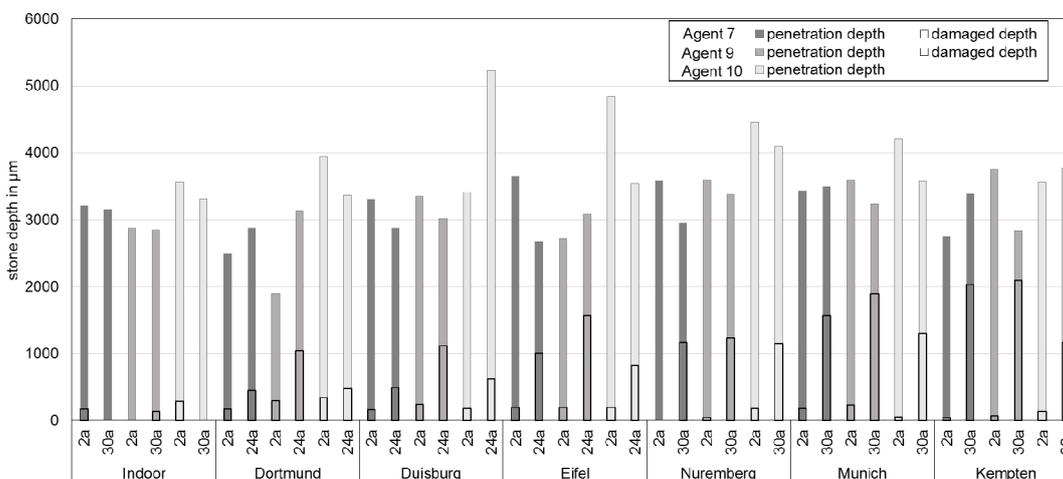
**Figure 13.** Comparison of the penetration depth of agents 3 or 4 applied on OKS with the damaged depth calculated with Equation (5) (depth 0 = surface of the stone).



**Figure 14.** Comparison of the penetration depth of agents 5 or 6 applied on OKS with the damaged depth calculated with Equation (5) (depth 0 = surface of the stone).



**Figure 15.** Comparison of the penetration depth of agents 8 and 11 applied on OKS with the damaged depth calculated with Equation (5) (depth 0 = surface of the stone).



**Figure 16.** Comparison of the penetration depth of agents 7, 9 and 10 applied on OKS with the damaged depth calculated with Equation (5) (depth 0 = surface of the stone).

## 5. Conclusions

The influence of up to 30 years of outdoor weathering at six different locations in Germany on the effectiveness of 11 different hydrophobic agents applied on Obernkirchener Sandstones is analysed in this paper. Periods of 24 and 30 years of outdoor weathering led to an ageing of the treated stone surfaces, expressed by discolouration and staining. By measuring colour changes, it could be shown that the formation of black crusts, the deposition of particles and biogenic growth caused a gradual darkening as well as significant changes in total colour over time. Beside the optical changes and colorimetry, the water absorption behaviour was investigated with two different methods: applying low pressure with the pipe method and capillary water absorption from a wet underlay. Afterwards, the test results were analysed with four different evaluation methods: calculation of the protection degrees  $PD_{LP}$  (from pipe method) and  $PD_{Ci}$  (from capillary water absorption) as well as of the velocity of water uptake during capillary water absorption measurements between 5 and 120 min and calculation of the damaged depth inside the stone using single-sided NMR technique.

It can be concluded that the degradation of the treated stones has been increased due to a longer weathering period of up to 30 years. This degradation can be illustrated with the damaged depth, which has been calculated from NMR measurements during capillary water absorption. The increase of the damaged depth leads to a higher velocity of water uptake and to a decrease of the protection degree  $PD_{Ci}$ . As long as the effective hydrophobic zone is three times the depth of the damaged area, the functionality of the hydrophobing agent is still given.

Only agents 2, 3 and 4 which are based on isobutyltrimethoxysilane show already after 2 years of outdoor weathering a clear loss of performance. The irregular distribution of these agents inside the matrix of OKS caused a high variation of the penetration depth, which partly led to a noticeable deterioration of the hydrophobic layer.

Comparing the protective agents containing siloxane, the low-molecular methylethoxysiloxanes (agent 5 and 6) show even with a low content of 7.5% (agent 6) a good performance, which is similar, partly better than the oligomer methylethoxysiloxane (agent 7). Especially after 30 years of outdoor weathering, the agents with oligomer siloxane based on an isooctylmethoxy-structure (agent 9 and 10) have a higher performance loss than the agents 5 and 6.

The effectiveness after 30 years outdoor weathering of the protective agents based on silicone resin is comparable to that of low-molecular siloxanes. Agent 8 shows a more reduced hydrophobic effect due to the low ingredient content and possibly to the isooctyl-structure.

Comparing the six different locations, it can be concluded that the degradation of the treated stones is higher in southern Germany than in North Rhine-Westphalia. This fact can be explained by a longer weathering time of 6 years as well as the rougher environment. In North Rhine-Westphalia, the rural location Eifel, which has a high amount of temperatures under 0 °C and relative humidity above 80% within one year, leads in general to a higher degradation compared to Duisburg and Dortmund.

To sum up, with the help of complementary evaluation methods, the durability of different hydrophobic agents applied on Obernkirchener Sandstone and under the influence of outdoor weathering can be analysed in detail. After 30 years, all agents show a decrease in performance, but some protective agents still provide an effective hydrophobic layer.

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