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Long-Term Studies on Polymer-Based Impregnation Agents on Natural Stones

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Abstract

Minerals in natural sandstones can lose coherence as a result of binder depletion or microcracking. Polymer-based impregnation agents have been developed with the aim of reducing this type of deterioration for natural stones in buildings and monuments. Prior to using these products on historic buildings, various tests on their effectiveness and durability need to be carried out. The problem of accelerated ageing methods is that they can induce material damage which is not comparable to processes occuring in nature. On the other hand, long-term outdoor exposure is time-consuming and costly. At the Institute for Building Materials Research an experimental apparatus called “VENUS” (German abbreviation for 'test chamber for the development of realistic environmental simulation') is used for accelerated, reproducible and complex weathering. The weathering cycle of the VENUS chamber described in this paper has been selected specifically to study the long-term behaviour of polymer-based impregnation agents applied to natural stones. To estimate the quality of natural simulation and the rate of acceleration in the VENUS chamber, additional outdoor weathering has also been carried out. Specimens with polymer-based impregnation agents were exposed to weathering in four different European climates (Duisburg (industrial), Eifel (rural), Corsica (marine), Wank (alpine)). The characteristic material parameters, such as elastic modulus, flexural strength, water absorption and water repellence, were determined on stone specimens exposed to field weathering for a period of approximately 10 years as well as on those specimens subjected to weathering in the VENUS chamber. The VENUS chamber represents changes in characteristic material parameters with a good degree of correspondence to natural weathering. The experiments carried out in this study have shown that the use of the VENUS chamber accelerated the ageing process by a factor of two in comparison with natural field weathering.

1 Introduction

Most of the German historic stone buildings and monuments were constructed with sedimentary stone. Their chemico-mineralogical composition and their physical structure, interspersed with capillary and nano-pores, limit their durability vis-à-vis weathering factors.

New types of polymer-based impregnation agents for stone have been developed in recent years in an extensive research project conducted in close cooperation with the chemical industry [1]. These impregnation agents penetrate deep into the capillary pore structure in liquid state and coat the inner pore walls with an ultra-thin, hydrophobic and elastic film. Quartz and other mineral constituents which have lost coherence as a result of binder depletion or microcracking are provided with a uniform coating and linked together via „polymer-grain bridges". Apart from stabilising the damaged grain skeleton, this treatment also prevents the penetration of liquid water and other harmful substances. Sealing the ultra-fine pores lowers the amount of moisture which is bound by adsorption and reduces swelling and shrinking processes. The larger pore channels remain open, and the permeability to water vapour is largely retained. In addition to comprehensive testing to establish the effectiveness of such agents [2], durability tests have also been carried out under complex simulated weathering conditions at the laboratory and in field conditions in various climates for the past 15 years. Some of these tests are discussed below.

2 Weathering methods

2.1 The “VENUS” environmental simulation chamber

The overwhelming majority of scientific publications dealing with weathering resistance of natural stone confirm the complex, overlapping effects of numerous factors acting on the stone and resulting in deterioration processes. Single-parameter laboratory tests provide only imprecise simulations of the processes which take place in nature and generally fail to supply any results which can be utilised for further material optimisation measures. Furthermore, it has been shown that accelerated experiments may lead to gross misjudgements of performance. These result from the excessive stress levels applied that result in processes which do not occur in natural weathering.

The key requirement in developing the VENUS environmental simulation chamber was that the multiple variable used in the weathering should follow the conditions (maxima, minima, ramps, combinations) found in natural conditions. A degree of acceleration is obtained by eliminating or reducing parameters that are known to have little influence on the deterioration processes. Thus, the main advantage of laboratory simulation is the possibility of generating reproducible damage corresponding to natural conditions, rather than the acceleration aspect.

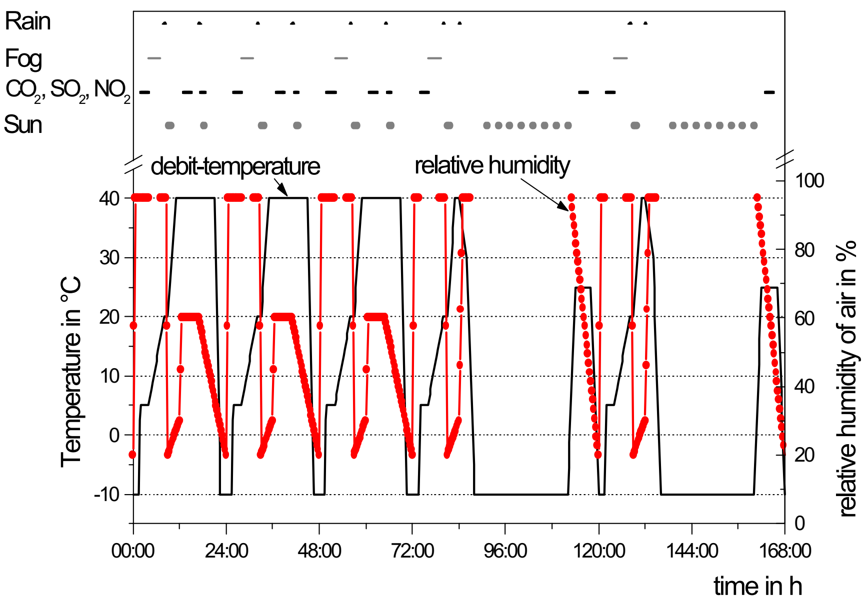

Figure 1: Weathering cycle in the VENUS chamber to induce damage in natural stones impregnated with protective polymers

The VENUS chamber enables to control the exposure of specimens to weathering elements such as sun, rain, freeze-thaw cycles, temperature changes, humidity changes and gaseous pollutants (SO_2, CO_2, NO_2). Condensation processes inside substances with capillary pores can also be controlled [3]. A one-week cycle covering all the stated elements was developed in interdisciplinary cooperation (Figure 1). This cycle represents weather elements of an average year in central Europe which, though extreme, nevertheless correspond to the naturally occurring characteristics in terms of minima, maxima and ramp gradients.

2.2 Weathering locations

To allow comparison between the test results obtained by laboratory wathering in the VENUS chamber with real, long-term exposure, freshly quarried samples, both treated and untreated, were deposited at the following field locations in 1990:

- In Duisburg (50m above mean sea level)
- In the Eifel region (530m above mean sea level)
- On the Wank mountain (1780m above mean sea level, Alps)
- In Corsica (30m above mean sea level)

Table 1: Climatic data for the field weathering locations, mean values over the respective weathering periods and those used in the VENUS chamber.

	Temperature			Freeze-thaw cycles	Global radiation
	< 0° C	> 25° C	> 30° C		
	T in h/a			1/a	KWh/m² a
Duisburg	481	292	59	57	970
Eifel	1070	71	3	72	1011
Corsica	33	850	-[1)]	-[1)]	1556
Wank	2540	0	0	198	1181
VENUS	1111	1515	759	1280	1656

	Precipitation			Pollution	
				NO_2	SO_2
	h/a	Times/a	mm/a	ppm	ppm
Duisburg	672	425	708	18,8	17,8
Eifel	929	541	944	6,6	7,2
Corsica	-[1)]	-[1)]	662	-[1)]	-[1)]
Wank	1126	386	1155	1,5	0,5
VENUS	130	520,0	12350	16,3	19,0

Table 1 shows the mean climatic data for the past 10 years at the above-stated field locations. An extensive evaluation of the climatic data for temperature and precipitation based on half-hour values has been carried out, in order to obtain information regarding annual precipitation times and precipitation frequencies, the duration of certain temperature levels and the number of freeze-thaw cycles. In addition, the climatic data used in the VENUS chamber related to a 7-year testing period is also included for comparison.

To allow the assessment of weathering effects on the deterioration of both treated and untreated stone specimens at different times, specimens were taken from the field locations after 1, 3 and 10 years for study in the laboratory. The weathered specimens from the VENUS chamber were removed after 0.5; 1.0; 1.5; 5 and 7 years. The test chamber ensured continuous weathering of the specimens.

Table 2: Main properties of the tested products

Product	Refer-ence	Solvent	Solid content	Density	Viscosity	Surface tension	Penetration depth	
							EH	SS
-	-	-	M.-%	g/cm³	Mpa*s	mN/m	mm	mm
PUR	87	Butyl-Acetate	27	0,9150	2,1	25,0	42	18
SAEE	89	Ketone	37	0,9488	1,3	26,2	49	19

3 Experimental

3.1 Materials

Two sandstones were selected for the study presented in this paper: Ebenheider sandstone (EH) and Sander sandstone (SS).

Two impregnating agents were tested. The first one is a polyurethane prepolymer, diisocyanate modified with alkyl polysiloxane (SSS 87). This agent reacts with moisture to produce long-chain polyurethanes (PUR) which form a continuous film. The second one is a silicic acid ethyl ester solution (SAEE) additioned with alkyl siloxane oligomers, (SSS 89). The SAEE reacts with water to eventually form amorphous silica gel. It may also bond to the sandstone through condensation with the hydroxyl groups on the mineral surfaces. The primary function of the silica gel is to stabilise loose zones in the natural stone. The added siloxanes serve to induce a hydrophobic effect, thus inhibiting the absorption of liquid water into the pore structure of the stone. Although this material does not form a continuous film, it was used as a reference product on the basis of its prolonged use in practice. Table 2 shows fundamental properties of the products tested.

3.2 Test Results and Discussion

3.2.1 Introductory remarks

The performance of the treatments was evaluated by the changes in contact angle both on the surface of the stone as well as in depth.

The influence of different weathering on both treated and untreated specimens was evaluated by changes in the mechanical parameters of the samples.

3.2.2 Contact angle

Changes in the contact angle served to assess the declining hydrophobic effect of the stone impregnating agents as a result of climatic influences. Tables 3 to 6 show the decrease in the contact angle over time and at various depths up to 11-mm. To

Table 3: Changes in contact angle (c.a.), Sander sandstone treated with SSS 87 (PUR)

Location	Slice 1 (0-4 mm)					Slice 2 (5.5-9.5 mm)					Slice 3 (11.0-15.0 mm)				
	Age t in years														
	1	1.5	3	7	10	1	1.5	3	7	10	1	1.5	3	7	10
VENUS	●	●		◐		●	●		◐		●	●		◐	
Duisburg	●		●		◐	●		◐		●	●		◐		●
Eifel	●		●		◐	●		◐		●	●		◐		●
Corsica	●		●		○	●		●		●	●		●		●
Wank	●		●		○	●		●		◐	●		●		◐

(c.a. >70° = ●; c.a. <70° and > 20° = ◐; c.a. < 20° = ○)

Table 4: Changes in contact angle. Sander sandstone treated with SSS 89 (SAEE+)

Location	Slice 1 (0-4 mm)					Slice 2 (5.5-9.5 mm)					Slice 3 (11.0-15.0 mm)				
	Age t in years														
	1	1.5	3	7	10	1	1.5	3	7	10	1	1.5	3	7	10
VENUS	●	●		◐		○	◐		○		◐	◐		○	
Duisburg	●		●		●	◐		●		◐	◐		●		◐
Eifel	●		●		◐	○		◐		○	○		◐		○
Corsica	◐		◐		○	◐		○		◐	◐		○		◐
Wank	●		●		◐	◐		◐		◐	◐		◐		◐

(c.a. >70° = ●; c.a. <70° and > 20° = ◐; c.a. < 20° = ○)

obtain the data for the different depths, the stone specimen was sawn into 4-mm thick slices parallel to the stone surface.

In the tables, black circles symbolise a good hydrophobic effect with contact angles larger than 70°, half black/half white circles indicate a discernible reduction in the hydrophobic effect with contact angles between 20° and 70°, and white circles denote loss of the hydrophobic effect, with contact angles smaller than 20°.

SSS 87 (PUR) penetrates more deeply and evenly into the stone pore structure than the silicic acid ethyl ester + siloxane solution irrespective of the variety of sandstone. For this latter agent, SSS 89 (SAEE+), chromatographic effects can lead to an accumulation of the added siloxane in the first slice, while the silicic acid ethyl ester solution penetrates more deeply into the pore structure.

Table 5: Changes in contact angle. Ebenheider sandstone treated with SSS 87 (PUR)

Location	Slice 1 (0-4 mm)				Slice 2 (5.5-9.5 mm)				Slice 3 (11.0-15.0 mm)			
	Age t in years											
	1	3	5	10	1	3	5	10	1	3	5	10
VENUS	●		◐		●		●		●		●	
Duisburg	●	●		●	●	●		●	●	●		●
Eifel	●	●		◐	●	●		●	●	●		●
Corsica	●	●		○	●	●		●	●	●		●
Wank	●	●		◐	●	●		●	●	●		●
(c.a. >70° = ●; c.a. <70° and > 20° = ◐; c.a. < 20° = ○)												

Table 6: Changes in contact angle. Ebenheider sandstone treated with SSS 89 (SAEE+)

Location	Slice 1 (0-4 mm)				Slice 2 (5.5-9.5 mm)				Slice 3 (11.0-15.0 mm)			
	Age t in years											
	1	3	5	10	1	3	5	10	1	3	5	10
VENUS	●		◐		◐		○		◐		○	
Duisburg	●	●		●	◐	◐		◐	◐	◐		◐
Eifel	●	●		◐	◐	◐		◐	◐	◐		◐
Corsica	◐	◐		○	◐	◐		◐	◐	◐		◐
Wank	●	●		◐	◐	◐		◐	◐	◐		◐
(c.a. >70° = ●; c.a. <70° and > 20° = ◐; c.a. < 20° = ○)												

A reduction of the hydrophobic effect for SSS 87 is discernible in the first 11-mm of the Sander sandstone in the specimens subjected to weathering both in the VENUS chamber and on the Wank mountain (Table 3). This reduction can be attributed to temperature effects. In contrast, the Ebenheider sandstone treated with this same product reveals a decline in the hydrophobic effect on the surface of the specimens only after 5 years' weathering in the VENUS plant and 10 years' exposure to outside weathering (Table 5).

The sandstone variety does not influence significantly the change of the hydrophobic effect for either impregnation agent. This means that the reduction in the hydrophobic effect on the surface is primarily a function of the climate, for example high radiation in combination with exposure to sea salt in Corsica leads to a reduction in the hydrophobic effect of SSS 89 (SAEE+) after only one year.

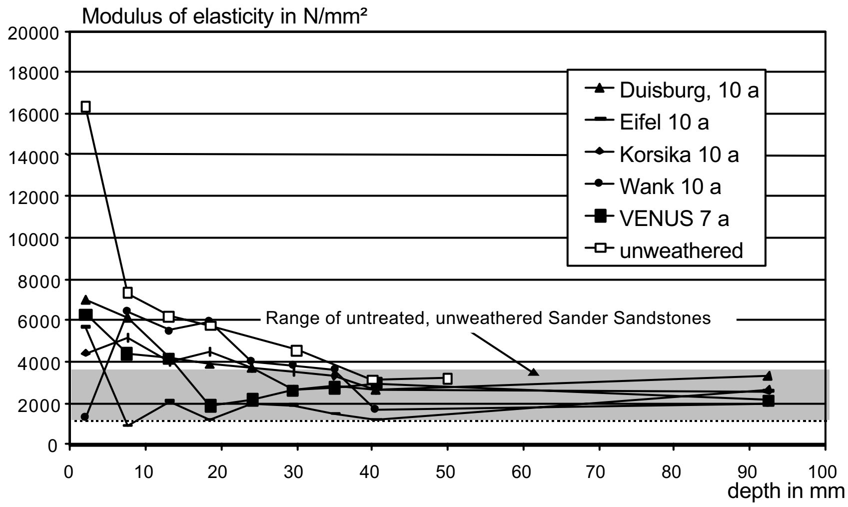

Figure 2: Depth profile of the modulus of elasticity of the Sander sandstone treated with SSS 87 (PUR)as a function of weathering location

The VENUS chamber reduceds the hydrophobic effect on the Ebenheider sandstone twice as fast as compared to the field locations in Eifel and Wank (see tables 5 and 6). The most severe loss of hydrophobic effectiveness occurs after 10 years of outside weathering in Corsica and could not be simulated in the VENUS chamber even after 5 or 7 years.

3.2.3 Mechanical properties

To evaluate the mechanical properties of both treated and untreated sandstones after weathering, biaxial bending tests were carried out on 4-mm thick slices. These were obtained at different depths by sawing the slices parallel to the surface. The modulus of elasticity and the tensile bending strength were determined on them thus obtaining a in-depth profile of these properties.

Figure 2 shows the modulus of elasticity at various depths of the Sander sandstone treated with SSS 87 (PUR) after 10-year weathering at field locations in Duisburg, Eifel, Corsica and Wank and after 7-year weathering in the VENUS chamber. In each case, the median derived from three individual values is shown, in order to compensate for variations due to heterogeneity in the microstructure of the stone. The range of an untreated, unweathered Sander sandstone is represented in the diagram by a bar with a grey background. The curve with empty boxes shows the median of three Sander sandstone specimens which were treated with impregnation agent but which remained unweathered.

Table 7: Reduction in the modulus of elasticity of the weathered specimens in relation to the corresponding unweathered specimens

Stone	SSS	Unweathered Modulus of elasticity	Duisburg	Eifel	Corsica	Wank	Nature	Venus
			Reduction in relation to the unweathered specimens (mean of slices 1 and 2)					
		N/mm²	%					
SS	-	2455	5	25	2	23	14	1 [1)]
	87	12035	42	71	63	67	61	59 [2)]
	89	16569	45	68	51	65	57	66 [2)]
EH	-	1953	0	0	21	0	5	38 [1)]
	87	27032	32	84	54	48	54	51 [1)]
	89	18586	26	71	57	35	47	58 [1)]

1) Weathering duration: 5 years
2) Weathering duration: 7 years

The moduli of elasticity of the weathered Sander sandstones are lower than those of the treated, unweathered Sander sandstones (Figure 2). After 10 years of field weathering, a substantial loss of elasticity can be observed in the first slice in particular. For specimens weathered on the Wank mountain the modulus of elasticity has declined to the level of the untreated sandstone. The characteristics of the modulus of elasticity over the stone depth of the specimens weathered in the VENUS chamber follows the characteristics of the specimens exposed to field weathering.

Table 7 shows the moduli of elasticity of the unweathered sandstones with and without treatment. The table also gives the percent reduction in the moduli of elasticity upon weathering as compared to the unweathered specimens. The column headed "Nature" shows the average percent reduction in the moduli of elasticity for the specimens subjected to field weathering. The mean value of this parameter as determined on the specimens from the four field locations provides a representative value for the different climates in Europe.

The table also shows that the reduction in the modulus of elasticity (mean of slices 1 and 2) is substantially greater for treated than for untreated specimens after 10-year weathering in field location and after 5 to 7-year weathering in the VENUS chamber. This pronounced reduction in the initial years can be seen as a positive characteristic, as temperature and moisture induced internal stresses may lead to damage if the outer area of a stone exhibits a high modulus of elasticity. The reasons for this pronounced decline in the modulus of elasticity need to be investigated further. For this purpose, field weathering of the specimens is being continued.

Table 7 shows that the reduction in the modulus of elasticity of treated weathered specimens as compared to unweathered specimens is similar to that induced in the VENUS chamber. This means that the weathering cycle applied in the VENUS chamber accelerates natural weathering by a factor of two. This cycle was specifically designed to enable investigation of the long-term effectiveness of stone impregnation agents applied to stone.

The reduction in the modulus of elasticity is only abount 8% higher for the treated Sander sandstones after 7 years than for the Ebenheider sandstones after only 5 years when weathered in the VENUS chamber. Thus, the loss of elasticity in these specimens under these conditions appears to be greater in the first 5-year weathering than in the subsequent two.

The situation is completely different for the case of untreated stones. The selected weathering cycle for the VENUS chamber is not suitable to evaluate the loss in elasticity of the untreated natural stones. For instance, 5-year weathering in the VENUS chamber corresponds to the climate in Duisburg and Corsica for the Sander sandstone, while the reduction in the modulus of elasticity is around 20% higher when exposed in the Eifel region or on the Wank mountain. On the other hand, the highest reduction in the modulus of elasticity for the untreated Ebenheider sandstone was obtained after 5-year weathering in the VENUS chamber. For untreated stones, the different properties of the materials have a substantially greater influence when comparing various field locations, than when evaluating treated stones. In the latter case the observed modulus of elasticity corresponds to the composite product-natural stone. To assess the deterioration of untreated natural stones, both the weathering cycle of the VENUS chamber and the investigation methods require to be adapted to the specific properties of a stone.

4 Summary and outlook

It was shown that for the stones tested, Sander and Ebenheider sandstones, treatment with the impregnation agent SSS 87 (PUR) resulted in a water-repellent effect of at least 11-mm deep into the stone. A decline in the surface hydrophobization of the specimens was observed with both agents tested, SSS 87 (PUR) and SSS 89 (SAEE+), after 10-year field weathering and 5/7 year-weathering in the VENUS chamber.

The reduction in modulus of elasticity suffered upon weathering by treated specimens, as compared to unweathered ones, is around 50%-60% for a “representative” climate of Europe. This is independent of the impregnation agents and the stone substrate.

The aim of inducing reproducible damage that corresponds to that resulting from natural weathering for two sandstones treated with two different impregnation agents was attained with the VENUS environmental simulation chamber. It was also shown to result in an acceleration factor of about two. However, the evaluation of weathering of untreated stone requires a different approach given their microstructure variations and the diverse effects induced by different weathering locations. The study is continuing with further field testing.

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