Hydrophobe III -

3rd International Conference on Surface Technology with Water Repellent Agents, Aedificatio Publishers, 203–218 (2001)

Experiments on the Compatibility of a Polysiloxane Treatment with Substrates Loaded with Sodium Sulphate: Influence of the Physical Properties of Substrates on the Salt Content Limit

A.Miquel¹, P. Bromblet¹, V. Vergès-Belmin¹, L. Binda², G. Baronio², E. De Witte³, H. De Clercq³, R. Van Hees⁴ and H. Brocken⁴ ¹Laboratoire de Recherche des Monuments Historiques

²Polytechnico De Milano

³Institut Royal du Patrimoine Artistique

⁴TNO Building and construction Research)

Abstract

Within the framework of an EC program on the compatibility of salt with surface treatments (SCOST), crystallization tests were carried out on 20 different substrates (limestone, sandstone, brick, tuffeau, tuff and plaster) treated with a polysiloxane (Rhône Poulenc H224) or untreated. First, the samples were treated with the hydrophobic agent and the impregnation depth and product consumption were measured. Crystallization tests were carried out for each material and with several initial salt contents. Both visual examination of the damage and the weight measurement of the loose materials (stone and salt) collected after the test (mass loss) were undertaken providing qualitative and quantitative test evaluations. The influence of the protective treatment on the deterioration observed depends on the type of substrat. In general, it gives rise to spalling or flaking worse than that observed for untreated specimens. The treatment modifies the way the substrate dries and prevents surface efflorescence formation. But as salts crystallise deeper within the porous network, the treated material suffers other degradation phenomena and eventually, more damage. For each type of substrate, the tests enabled to determine a salt limit content, i.e., the highest sodium sulphate content for which no damage was observed during the crystallization test. No clear correlation could be established between any given parameter of the studied substrates, such as mechanical strength, porosity, capillarity, etc. and the salt limit content or the intensity of the observed deterioration. Finally, an attempt is made to analyse the results by means of a statistical approach. Parameters used were the physical properties of substrates, their nature (limestone, sandstone, brick...), the impregnation depth and consumption of the treatment, the intensity of the damage, the salt limit content and the damage appearance time.

Experiments on the Compatibility of a Polysiloxane Treatment with Substrates Loaded with Sodium Sulphate: Influence of the Physical Properties of Substrates on the Salt Content Limit

1 Introduction

Water repellent treatments are used to protect buildings against water. Their application can be beneficial and provide protection to masonry if the walls are not contaminated with salt or subjected to an interior water source such as a capillary rise of underground water. But during the life of a monument, it would be exceptional for a structure to remain exempt of salts, infiltrations or any other potential source of water. Thus, a treatment applied on a salt-laden masonry may present degradation risks, salts may crystallise underneath the treated layer and cause its detachment. The main objective of the Salt Compatibility Of Surface Treatment European Program is to determine the admissible salt content limit for selected materials treated with a water-repellent. The present paper focuses on the effect of a single treatment (Rhodia H224) and the resulting damage to the various materials studied when subjected to different initial sodium sulphate contents. First, crystallization tests were carried out with different initial salt contents in order to determine the maximum sodium sulphate limit below which no damage occurs. Results were evaluated through visual examination and by measurement of the mass-loss of the collected substrate and salt. Then, to better understand the causes of decay following salt crystallization in the presence of the treatment, the tests results (substrate loss, collected salt, time of damage appearance) were analysed by means of a statistical approach taking into account the physical properties (structural, hygric and mechanical properties as well as the mineralogical composition), and both the treatment impregnation depth and consumption.

2 Crystallization tests

2.1 Remarks

The salt crystallization tests on individual materials were carried out for 20 substrates with different concentrations of sodium sulphate salt and also in combination with the water repellent.

2.2 Substrates

Twenty substrates were selected according to their representativeness in each European program partner country: 1 plaster, 1 tuffeau, 1 tuff, 4 bricks, 9 limestones and 4 sandstones. Some properties (porosity, capillary moisture content *C.M.C*, capillarity coefficient *A*, ionic conductivity γ , dry and saturated mechanical resistances σ_{dry} , σ_{sat}) were first determined (Table 1). The capillary test was measured in parallel to the stone bedding planes as performed at the LRMH. The samples were then subjecteded to splitting tests by the P.D.M.

							I	
Substrate	Code	Size cm ³	Porosity	C.M.C	А	γ	σt dry	ot sat
		L*W*H	% (g/cm3)	% (g/g)	g/cm ² /.h ^{0,5}	(µS)	MPa	MPa
Plaster	PL	10*5*10	46	46	6,79	1896	0,49	
Tuffeau	AU	10*5*10	42	28	3,79	151	0,86	0,39
Tuff Stone	TU	18*4*8.5	35	25	1,70	119	1,39	0,79
Bricks								
Red Brick	RB	18*4,3*8,7	26	16	3,05	56	3,94	2,76
Roborst	RO	19*8,6*6,1	20	11	2,54	66	1,3	1,08
Yellow Brick	YB	18*3,9*8,7	31	19	2,16	228	2,22	1,34
Soft mud brick	SMB	25*5,2*12	35	22	1,97	1550	1,06	0,99
limestones								
St Maximim	MX	10*5*10	31	16	4,11	131	1,21	0,98
Migné	MI	10*5*10	27	13	1,64	97	2,69	1,56
Lavoux	LA	10*5*10	26	13	1,43	131	1,45	0,96
Noto	NO	10*5*10	26	14	0,94	128	2,65	0,91
Courville	СО	10*5*10	23	10	0,39	171	3,76	1,84
Savonnières	SA	10*5*10	18	10	0,55	145	1,347	0,953
Massangis	MA	10*5*10	12	5	0,22	121	5,39	3,33
Euville	EU	10*5*10	9	4	0,59	123	2,28	2,21
Balagem	BA	10*5*10	4	1	0,04	133	7,8	5,56
Sandstones								
Molasse bleue	MB	10*5*10	15	5	0,25	154	2,01	0,66
Grès à Meule	GM	10*5*10	15	7	0,90	116	4,07	2,96
Ferruginous	FS	10*5*10	14	4	0,59	115	3,56	3,04
Serena	SE	10*5*10	4	1	0,03	166	10,11	5,13

 Table 1:
 Substrate Properties

2.3 Treatment

The treatment is the solvent-based water repellent H224 (polysiloxane) diluted to 10% with white spirit. The samples were impregnated on one side (in a parallel to the bedding) by capillarity during a 10-second contact time with the diluted water repellent.

2.4 Salt solution concentrations

Sodium sulphate solution concentrations were selected according to the capillary moisture content (CMC) of each substrate.

If CMC > 10% : C1=1%, C2=2.5% C3 = 5%

If CMC <10% : C2=2.5% C3 = 5%; C4=7.5%

The substrate was allowed to absorb an amount of solution equal to 80% of its CMC in order to ensure total absorption by the treated specimens.

Three samples were prepared for each salt concentration-treatment combination. Thus, at least 24 samples were prepared for each type of substrate. Sometimes, the initial salt concentration had to be decreased to 0.25% or 0.63% or increased to 7.5% or 10% in order to determine the limits of admissible salt content.

2.5 Crystallization tests

The salt was introduced into the substrates by capillary absorption in parallel to the bedding. When all of the solution was absorbed, they were sealed into a box with only the top of the sample showing and exposed to 50% R.H and 20° C for its drying. A visual and photographic survey of the damage was carried out. When there was no damage, a new cycle was started with only water. When damage occurred, the mass loss was collected by brushing and filtering to separate the salt from the damaged substrate. With this method, the damaged substrate and the salt included in the damaged part were collected.

3 Results

3.1 Treatment: Consumption and depth impregnation

The average water repellent consumption C_{H224} (g/m²) was evaluated by weighing. The samples were broken at right angles to the treated surface and the crosssection was put into contact with water for a few seconds. Then, it was possible to roughly determine depth impregnation D_{H224} (mm) by measuring the observed thickness of the dry layer. Impregnation depth increases with consumption (Fig 1). However, materials could be differentiated into 2 groups. The first one composed by AU, MX and PL , while the second group includes all the other materials.

3.2 Damage: qualitative evaluation using visual examination

The terms used for the description of damage were based on the definitions in [1]. Among the 9 limestones, 7 were damaged with the lower initial salt concentration used (C1) so new samples were prepared using concentrations of 0.25% or 0.625%. The most serious damage was observed on MX which showed largest impregnation depth of all: 7 mm. Then came NO, LA, SA and MI. On the untreated samples, the most frequent kind of observed damage was scaling or exfolia-



Figure 1: C_{H224} in relationship to D_{H224}



Figure 2: Crystallization : observation

tion. On treated samples, spalling was more frequent (Fig 2). Different types of damage were observed depending on limestone granulometry. For example, the damage on untreated MI appeared as thin successive flakes perpendicular to the bedding, but as crumbling in the case of untreated SA. So far, the 2 limestones (EU and BA) with lowest CMC have not shown any damage within the initial salt content range examined. Bricks (except RO, and all of the untreated samples without surface disintegration but with salt efflorescence) were damaged with different ini-

tial salt contents. On untreated bricks, the damage appeared as crumbling. On the treated samples, as detachment of part of the surface and as crypto-efflorescence just below the treated part. Concerning sandstones (except the lowest-capillarity SE), they were all damaged, GM in particular. Untreated sandstones showed scaling and sometimes splitting. For treated sandstones, bulging was first noticeable followed by spalling. TU was visually more damaged than AU. Plaster, the material with highest CMC, behaved differently from all other materials: it showed the highest impregnation depth as well as the highest initial salt content for deterioration. For untreated PL samples, all the salt migrated with the liquid flow to the top and crystallised outside the solid matrix whilst treated samples only showed powdering as if the treatment had protected it.

For each type of material except plaster, by the time damage can be visually observed, it appears that the degree of deterioration is more serious and important for treated than for untreated samples.

3.3 Time of damage appearance

Damage occurs more slowly on treated than on untreated samples due to the liquid water barrier of the treatment. Nevertheless, depending on the substrate, the difference in time of damage appearance between treated and untreated materials can differ greatly for the same amounts of added water since the drying time required to reach hygroscopic equilibrium at 50% RH can vary from a few weeks to several months. The treatment does not have the same consequences on all of the substrates. The relationship between the time of damage appearance and initial salt contents is as follows:

- On untreated samples: the time of damage appearance decreases or remains the same as the initial salt content is increased.
- On treated samples: the time of damage appearance decreases as the initial salt content is increased but it always remains above the time of damage appearance of untreated samples.

3.4 Salt limit contents for each substrate

The salt limit contents which appear in Table 2 were obtained over a one year period after the beginning of the crystallization tests. The second and third columns contain the 2 initial salt content values (salt mass/sample mass) for Ci delimiting the admissible salt limit content for a treated substrate. The lowest value C_m , indicates an absence of degradation and the highest value C_M damage. The fourth column presents the mass loss percentage in g/g (collected mass/initial sample mass) for the untreated (REF) and the treated (H224) sample. Last of all, our appreciations regarding treatment behaviour appear in the fifth column.

Code $C_m %g/g$		C_M %g/g	Collected Substrate %		Treatment benefit	
	Nothing	Damage	REF	H224	after 1 year	
PL	> 2,3		0,01	0,02	٢	
TU	0,6	1,3	0,8	0,9		
AU	0,3	0,7	-	0,1	8	
RB	0,4	0,8	0,2	20	8	
RO	> 0,5		0,01	-	٢	
YB	0,95	1,25	2,44	-		
SMB	0,5	1,1	1,22	6,2	8	
MX	0,05	0,2	-	0,4	8	
MI	0	0	-	0,02	[⊗] Incompatibility	
LA	0	0	-	0,02	Incompatibility	
NO	0,03	0,1	0,07	0,8	8	
СО	0,2	0,5	0,2	0,7	8	
SA	0,03	0,1	0,01	0,1	8	
MA	0,2	0,3	0,4	1,5	8	
EU	> 0,3		0,02	-	٢	
BA	> 0,08		-	-	٢	
MB	0,2	0,3	1,2	4,5	8	
GM	0,4	0,6	0,65	6,7	8	
FS	0,2	0,3	0,02	1,7	8	
SE	> 0,05		-	-	٢	

 Table 2:
 Crystallization test results : admissible Sodium sulphate content



Figure 3: Treated and untreated substrates: mass loss difference as a function of initial salt content

After a one-year period a provisional classification of the different types of substrates can be established on the basis of salt content limit, obviously limited to sodium sulphate and the H224 treatment:

Limestones ([0,1-0,3]% g/g, average $\approx 0,1\%$).< Sandstones ([0,2-0,3]% g/g), Bricks [0,2 - 1]%, < Tuff, tuffeau ([0,4 - 0,8]%g/g) < Plaster (>2,3%g/g) For the case of bricks, the results vary greatly depending on their type.

3.5 Mass loss due to the treatment with regards to the initial salt content

The difference of substrate loss between untreated and treated samples ($M_{sub,H224} - M_{sub}$) as a function of the initial salt content was plotted (Fig 3) to elucidate the influence of the degree of salting on the damage for each material.

For limestones and for the same amount of salt, the difference of mass loss of MX due to the treatment(6000 g/m^2) is higher than for other limestones according to visual examination. Its alteration depth corresponds to the impregnation depth of H224. The LA and NO stones both show similar differences in mass loss and they behave in the same way. For bricks except for RO, the mass loss at different salt contents reaches a higher constant value (15000-30000 g/m²). This increase in degree of deterioration is proportional to the impregnation depth as in the case of



A.Miquel, P. Bromblet, V. Vergès-Belmin, L. Binda, G. Baronio, E. De Witte, H. De Clercq, R. Van Hees and H. Brocken

Figure 4: Treated and untreated substrates: collected salt difference as a function of initial salt content

limestones. The YB mass loss is lower than for RB whilst the admissible salt limit for these 2 bricks is really different (it is more important for YB which shows a lower capillarity coefficient and higher mechanical resistance than RB). Furthermore, the drying time to reach hygroscopic equilibrium is higher for YB (7 months) than for RB (2 months). AU shows a higher difference in mass loss than TU contrarily to what can be visually observed. PL does not show any significant difference and its mass loss remains very low (30-40g/m²) in comparison to other substrates.

In each category, all of the treated samples lost more mass than the untreated samples and the mass loss increased with increased initial salt content.

In summary, it can be said that the presence of sodium sulphate is dangerous even at low concentrations when a treatment with H224 is considered.

The substrate classification in terms of mass loss is as follows :

Plaster < Tuff, Tuffeau < Limestones < Sandstones < Bricks

3.6 Salt loss with regards to the initial salt contents

As previously, the difference of salt loss between untreated and treated samples $(M_{salt,H224} - M_{salt})$ as a function of the initial salt content was plotted (Fig 4) to study the influence of the initial salting degree on salt crystallization.

As can be seen this difference is negative for most substrates: less salt was collected from treated than from untreated samples.



Figure 5: Mass loss difference (M_{subH224} - M_{sub}) as a function of depth impregnation

For untreated plaster samples, whatever the initial salt content was, 94% of the initial salt content was collected whereas few salt was collected from treated samples. However, for some substrates (MX, CO, MI, SA, FS, RB), more salt was collected on treated samples than on untreated samples.

The results are in accordance with the difference in mass loss: the percentage of substrate loss increases with the percentage of collected salt.

4 Discussion

From the results obtained from both treated and untreated samples (Fig 5), it is clearly evident that the impregnation depth accounts to a large extent for the difference in mass loss ($M_{sub H224} - M_{sub}$).

In most cases, from the quali- and the quantitative evaluations (Fig 6), the type of damage is more serious and significant on treated samples than on untreated samples whilst the collected salt is less important in the case of treated samples (Fig 7).

• On untreated samples, the drying of the liquid salt solution near the surface generates the formation of efflorescence without significant damage. The crystallization and growth of salt occurs mainly on the surface of the substrate. The collected amount of efflorescence increases linearly with the initial salt content. Salts come to the top of the samples



Figure 6: Untreated and treated: mass loss



Figure 7: Untreated and treated: collected salt

and crystallize in an 'open volume'. They reach the top of the sample by liquid flow migration. The most frequent damage patterns are powdering and crumbling.

• By comparison, the main damage on treated samples consists in the detachment of the treated thickness (MX, TU, RB, YB, FS, MB,...). This detachment can be thicker than 1,5 cm depending on impregnation depth and salts appear under this treated layer (growing as a crypto-flo-

rescence). During the drying process, the salted solution reaches to below the treated layer which forms a barrier to the liquid, and consequently to the salt, thus concentrating the salt solution. Drying continues only by slow evaporation as water vapour diffuses through the treated part of the material, allowing the solution to become highly supersaturated. The crystallization pressure generated (according to Correns' equation) can reach very high values because it is proportional to the supersaturation concentration of the solution. From Correns's equation, crystallization pressure, even for a supersaturation ratio as low as 2 at 20°C developed by thenardite (32MPa) or even mirabilite (8MPa), is high in comparison to the tensile strength of the materials (Table 1, σ_t <10MPa) as reported elsewhere [2]. This crystallization pressure is responsible for detaching the treated part. Nevertheless, in the case of PL, no alteration was observed despite its high initial salt contents, impregnation depth and CMC.

In crystallization tests, as mentioned by Rodriguez-Navarro and Doehne [3], it is not clear whether either or both factors are discriminating:

- the high supersaturation rate reached through rapid evaporation,
- the crystallization of thenardite instead of mirabilite (as the crystallization pressure of thenardite is higher than that of mirabilite for the same supersaturation).

An investigation of the effect of salt with regards to pore size distribution was studied by Rossi Manaresi and Tucci [3]. The authors show that 'before assuming the presence of salts to be harmful, the pore structure of the stone should be examined'.

Factors influencing stress development and cracking have been presented in recent works [5]. Added to the supersaturation of the salt solution, other factors are discussed such as pore size, interfacial energy (pore wall/crystal) and crystal form. As pointed out in this same study "even when the crystallization pressure is large, the stress existing in a single pore cannot cause failure because it acts on too small a volume. For fracture to occur, the crystals must propagate through a region of the network large enough that the stress field can interact with the large flaws that control the strength" [5].

Concerning the depth at which damage occurs, the following hypothesis was verified by the drying kinetics during crystallization test. The migration of ions to the drying surface depends on the liquid potential difference which is governed by the salt solution inside the pores. In the substrate, the higher the hygric potential difference, the higher the liquid permeability and the more salt can migrate to the surface. Water evaporation and salt crystallization mainly occur outside and the solution front moves towards the surface because of capillary sources.

	Untreated samples		Treated samples		
Correlation	>0	<0	>0	<0	
Collected Salt	-Ci -Porosity -VII/VI - Time appear.	-Volumic mass - pore radius: (r > 50μm)	-Ci -Time appear.		
Collected Substrate	- Ci, - Pore radius: (0.1 <r <1)<br="" μm="">-Time appear.</r>		-Ci -D _{H224} -Pore radius: (2 <r <7)<="" td="" μm=""><td></td></r>		

Table 3: Statistical analysis : correlation table

Furthermore, with a liquid barrier, drying kinetics and consequently time of damage appearance depend on the water vapour transfer through the treated thickness.

To complete the research and to attempt to understand the observed differences, correlations between substrate properties and crysallization test responses are investigated. This is done by means of a statistical analysis where the entry parameters are the nature of the substrate, its properties (Table1), treatment consumption, impregnation depth and initial salt contents (Ci). Also considered is the pore distribution, as determined with a mercury porosimeter, that is divided into 8 classes of pore sizes from number I ($r < 0,009\mu m$) to number VIII ($r > 50\mu m$).

Crystallization test responses are the collected substrate and collected salt percentages. The main results appear in Table 3. Both test responses are positively correlated with the initial salt content Ci, whatever the treatment. Nevertheless, for treated samples, the correlation between test results and substrate properties is less significant than for untreated samples. For untreated samples, the collected salt seemingly decreases as the percentage of macro-pores ($r>50\mu m$) increases.

The mass loss difference ($M_{subH224}$ - M_{sub}) is only caused by the treatment.

With regards to limestones, the mass loss of untreated samples is apparently significantly correlated to the salt content (C_M) and porosity. The mass loss of treated samples is seemingly significantly correlated to CMC, to the capillarity coefficient (A), to porosity and to consumption C_{H224} .

5 Conclusions

As a conclusion it can be said that the water repellent treatment in the presence of sodium sulphate increases the degree of deterioration in direct proportion to the impregnated volume.

When all the conditions generating salt migration inside the pore structure towards the surface are met, the treatment forms a salt and liquid barrier. The salt concentration beneath the treated area leads to crystallization inside a closed volume.

The admissible salt limit contents generally accepted by limestones is very low ($\approx 0.01 \% \text{ g/g}$) in comparison to the other substrates.

The characteristics of the materials that seem to better tolerate sodium sulphate with the treatment must either be:

- a low porosity mainly formed of very big pores $r > 7\mu m$ and with a low capillarity coefficient and a high mechanical resistance (like EU, BA); or,
- a high porosity formed by many small pores, resulting in a high capillarity coefficient, such as presented by Plaster.

6 References

- 1. R.P.J Van Hees, S. Naldini, Masonry Damage Diagnostic System, International Journal of Restoration of Buildings, (Nov 1995), vol 1, n°6, p 423-435.
- 2. A.Goudie & H.Viles : Salt weathering hazards Mechanisms of salt attack p123-156 (1997)
- 3. C.Rodriguez-Navarro & E.Doehne: 'Salt weathering : influence of evaporation rate, supersaturation and crystallization pattern' Eath Surf. Process. Landforms 24191-209 (1999)
- 4. R.Rossi-Manaresi & A.Tucci: Pore structure and the disruptive or cementing effect of salt crystallization in various types of stones- Studies and Conservation 36 p53-58 (1991)
- 5. G.Scherer: Crystallization in pores Cement and Concrete Research 29 p 1347-1358 - (1999)