

Brick-Wall Masonry Decay Patterns and In Situ Evaluation of the Effectiveness of Treatments of Torre Alberaria in Venice

V. Fassina¹, M. Favaro² and D. Melica³

¹Soprintendenza ai Beni Storici Artistici ed Etnoantropologici per le province di Venezia, Belluno, Padova e Treviso, Venice, Italy

²CNR-Istituto Chimica Inorganica delle Superfici (ICIS), Padova, Italy

³Istituto Veneto per i Beni Culturali, Venice, Italy

Abstract

In the framework of the European Project ASSET n. EVK4-2000-00572 "Assessment of suitable products for the conservative treatments of sea-salt decay", the effectiveness of some selected products intended to be used as water repellents and consolidants on the brick-wall masonry located in a costal environment and damaged by salt crystallisation due to different salt-sources was evaluated.

These products were applied on the wall masonry of Torre Alberaria in Venice and were tested by in situ measurements of water absorption. Furthermore to evaluate the penetration and distribution of the products and to investigate their interaction with soluble salts Scanning Electron Microscope (SEM) observations were carried-out on samples collected from the building.

Decay and weathering patterns were also considered in relation to the influence of flood tide, rising damp, marine spray and atmospheric pollutants.

Keywords: sea salts, rising damp, flood tide, water repellent, in-situ water absorption measurements

1 Introduction

Several monuments located in Venice marine environment have been selected in order to identify and describe the decay phenomena due to sea salts. A more detailed investigation on the characterization of physical, chemical and mineralogical properties of brick-wall materials related to weathering processes was carried out in Torre Alberaria, located at the Venice's Arsenale, which represents a typical example of a building exposed to the influence of flood tide, rising damp, marine spray and atmospheric pollutants.

In coastal areas, like Venice, where the sea level changes the problem of flooding is acute. According to particular meteorological conditions periodical and recurrent flooding phenomena takes place.

Rising damp phenomenon is due to the capillary transport of water from the superficial levels of the subsoil and/or water due to inefficient draining. Rising damp usually lead, in presence of salts, to different decay patterns. In general, the ground water gives rise to surface phenomena extending along all the walls of the building and having a persistent character (stains, moulds, erosion of stone etc.). Sometimes rising damp shows an irregular distribution of the moisture and of the damage in the wall due to the heterogeneity of porous materials constituting the brick-wall masonries. The height and the relevance of the rising damp phenomenon is also related to the type of material composing the masonry. The moisture content due to rising damp decreases from the lower to the upper level of the masonry and is distributed across the whole thickness of the walls, more relevant in depth than on the evaporation surface. Its height tends to be considerably reduced close to the surfaces where evaporation occurs, above all in correspondence with the most ventilated areas.

The emission of sea-salt particles from the sea is one of the most relevant sea-salt sources. Marine aerosols can be transported at a long distance from sea into the inland and they are removed from the atmosphere by wet and dry deposition processes. The enrichment of sea-salt by sea spray in historic monuments has been going on continuously over long periods of time. Accumulations found today are the result of sea salt deposition beginning at the time of construction of the building (Figure 1).

In relation to the different salt sources mentioned above, the location (height, orientation, etc.) of the sampling and of the measurements carried out in the case studies was defined: the sampling zones were selected in order to have, for each sampling zone, one main source of salt. In relation to the specific case study, samples were taken in the sea flooding area (generally under 0,80 m of the medium sea level), in zones with prevalent rising damp (usually between + 0,50 and +3,00 m) and in places where only marine spray was present (most of the times over + 7,00 m) [1].

To obtain useful information about the decay patterns, the following criteria were taken into account: quantitative and qualitative determination of salt and moisture contents according to visual evaluation of the condition of the wall.

Regarding areas affected by rising damp drilling cores at different heights along a vertical line as well as at different depths were made in order to evaluate vertical and horizontal distribution of moisture and salt contents in the wall-brick masonry.

In relation to possible sources of moisture and sea salts, different zones have been identified in the masonry. For each of these zones, having different moisture and sea salt load, recurrent decay patterns have been recorded [1]:

a) sub-tidal zone: situated under the limit of the mean level of the low tide. This area is characterized by: i) constant presence of water that prevents high concentration and accumulation of salts; ii) absence of serious salt crystallization damage; iii) presence of decay on the mortar joints, consisting mainly in the loss of material;

b) inter-tidal zone: located within the limits of the mean high and low tide. This area is characterized by: i) cyclic presence of water causing cyclic processes of dissolution/crystallization of marine salts, main responsible of the decay; ii) chemical attack of the masonry; iii) physical-mechanical action of the water causing loss of cohesion and consequent decrease of the mechanical strength of the bricks;

c) supra-tidal zone: above the mean high tide level. This area can be divided in three sub-zones:

c.1 rising damp: situated in the lower part of the wall, above the ground level. This area is characterized by high moisture and salt content. In this area a vertical distribution of the salts according to their solubility is surveyed: the most soluble salts accumulate at the upper fringe of the rising damp zone, whereas the less soluble crystallize already in the lower part of the wall [2]. Due to the evaporation process, salts accumulate in the outer layer of the material. The crystallization pressure developed results either in powdering/sanding of the substrate or, especially in case the material is not homogeneous (as e.g. presence of water repellent layer, gypsum crusts etc.) in scaling/spalling;

c.2 sea salt spray: located in the highest part of the building. These areas are affected by sea salt spray, either transported by rain and wind, or due to humidity condensation from air or fog. Processes of dissolution and crystallization of salts on the exposed surface and migration of salts towards the inner parts of the structures take place in these zones. These processes result in decay of the material, mainly consisting in powdering, sanding or scaling due to chemical and physical-mechanical actions;

c.3 flooding events: these areas are extended to the height reached by sea water during the flooding. They are distinguished by a high salt content and by serious decay that can go on for a long time if a moisture source is present (even if due only to high RH of the air).

Decay patterns for bricks are strongly dependent on the textural characteristics which are in turn related to the composition of the original clay and to the production processes and they play an important role in the weathering. The pore size distribution as well as the presence of the preferential orientations planes affect the seriousness and the distribution of the sea salt decay.

The decay patterns observed on Torre Alberaria are strongly dependent on the exposure and the south side shows more extensive decay than the north one. The tower is affected by rising ground water on the lower part, while on the upper part is subjected to strong ventilation and therefore affected by the marine aerosols transported by the wind, and occasionally the basement is subjected by high tide phenomenon (Figures 2 and 3). Notwithstanding a replacement of the first layer of bricks with new ones has been carried out in the past, strong decay phenomena are still in progress, with partial disruption or missing of bricks in correspondence to the area of salt crystallization.

To better quantify the deterioration phenomena, other parameters should also be considered (microclimate, techniques of construction, age of the building, etc.). It is nevertheless possible to define the problem and obtain significant data focusing the research on constituent materials and two fundamental parameters related to the phenomena of sea salt decay: moisture and soluble salt content.



Figure 1: Salt efflorescences on bricks surface



Figure 2: Weathering from marine spray on brick surface

2 Experimental part

To characterize weathering and decay processes in relation to exposure and different sources of sea water (flood tide, rising ground water and marine aerosols) the following measurements were carried out: qualitative and quantitative analysis of soluble salts [3] by ion chromatography; X-ray diffractometry (XRD) to identify mineralogical phases; porosity and pore size distribution [4] from outmost brick surface.

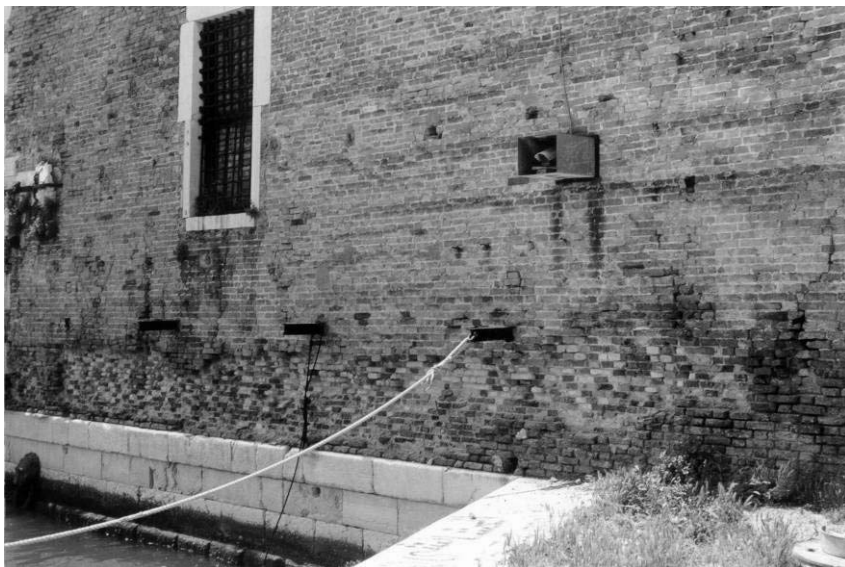


Figure 3: Torre Alberaria, south exposure: visible damage in the supra-tidal zone where rising damp is active

The study focused on southern and northern walls of the Torre Alberaria by taking the samples (powder or small flakes) from the surface, up to a maximum of 1 cm of depth.

After the removal of soluble salts from the substrate, some low-pressure water absorption measurements were performed [5]. Scales and cross sections taken from the building have been observed by scanning electron microscope (SEM) to evaluate: i) the surface morphology of applied products, ii) the penetration in the pores of different size, iii) the interaction with marine salts. The distribution and interaction of applied products and soluble salts were observed by X ray maps of selected chemical elements. Investigations were performed by a SEM Philips Model XL 40 LaB6; X ray maps for different elements were obtained using an EDAX DX Prime X-ray Energy Dispersive Spectrometer, V=25 keV.

3 Results and discussion

3.1 Decay and weathering characterization in relation to sea source and exposure

In high tide zone, chlorides (mostly sodium chloride, halite) reach the maximum concentration, 4.7 %, at 50 cm. height on both north and south sides, which means that the tide wets both sides of the basement with the same frequency, while sulphates at the same height is more abundant on the north side in respect to the south one (respectively 2.7 and 0.8 %). Such phenomenon is probably due to the slower water evaporation occurring on the north side which maintains the surface more moist thus favouring the process of sulphation on the surface. On the contrary, on the south wall, where unsheltered surface is more exposed to the wind and sunlight, the interaction between the substrate and the atmospheric pollutants is limited. This hypothesis is confirmed also by the XRD semi-quantitative determination of high quantities of gypsum, the only mineralogical phase of sulphates present. In the area interested by rising groundwater, data obtained show that the concentration of soluble salts largely depends on the exposure: in the south wall, chlorides concentration is generally greater in respect to the north one (4.5 and 2.7 % respectively at 100 and 150 cm height). Moreover in the south, the rising groundwater reaches lower height in respect to the north one. Such behaviour is closely related to the more effective process of water evaporation taking place on the south wall that is mainly exposed to sunlight and strong winds (Figure 4). Sulphates, identified as gypsum and



Figure 4: Concentration of chlorides at different heights

bassanite, are found in greater concentration at higher elevation compared to chlorides, in particular at 200 cm height, sulphates is present at 3 and 1.4% on the north and south side respectively indicating that sulphation process is probably prevailing with respect to the contribution of rising damp (Figure 5).

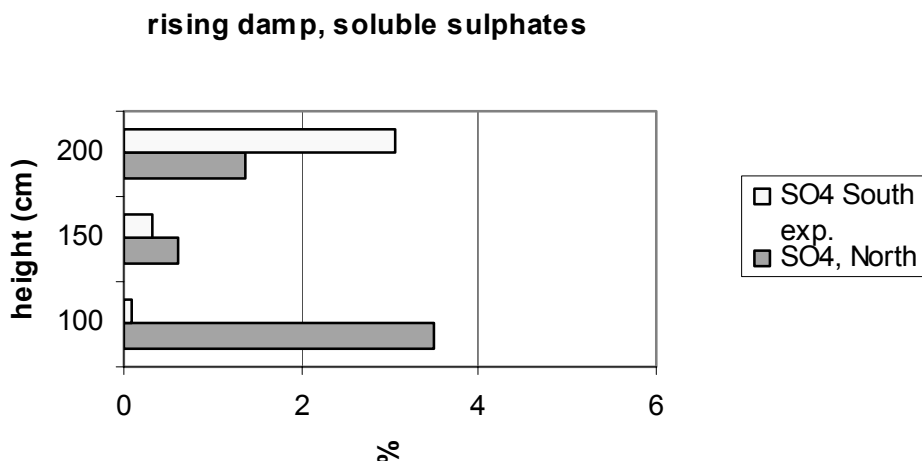


Figure 5: Concentration of sulphates at different heights

Table 1: XRD data obtained from samples collected at different exposure

sea salt source	sample	gyp	bas	Hyd	hal	bish	eps
Aerosol	TA-brick 1				x		
	TA-brick 2				x	x	x
	TA-mortar 3						
	TA-brick 8	x		Xx			
	TA-brick 9				xx		
rising damp	TA-brick 4	xxx		-		x	
	TA-brick 5	xxxx	x	x			
	TA-mortar 6						
	TA-stone 7						
	TA-brick 6	xxxx	xx				
flood tide	TA-brick 10					x	
	TA-brick 11				xx		
gyp= gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		hyd= hydrophyllite CaCl_2			bish= bishofite $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$		
bas= bassanite $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$		hal= halite NaCl			eps= epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$		

Regarding the area affected by marine spray, the only reachable side is the northern wall; it shows low concentrations of chlorides (less or equal to 1%) and quite higher concentrations of sulphates (10-30 %). This is due to the high solubility of chlorides, which are easily washed by rainwater and from the processes of sulphation which make the presence of sulphates more predominant compared to the other salts.

The chlorides are present as magnesium and sodium salts, respectively halite and bishofite, while the sulphates are present as gypsum and epsomite (magnesium sulphate eptahydrate).

3.2 Porosimetric measurements in relation to soluble salts

Mineralogical analyses performed on thin sections indicate a strong compositional heterogeneity of the examined bricks, ascribed to the different composition as well as to the different firing temperature. XRD analyses allowed the identification of mineralogical phases produced by firing and not detectable by optical microscope. On the basis of the analyses performed on these bricks, it is possible to recognize four groups characterized by different structural typologies.

Laboratory tests show that capillaries smaller than 0.1 μm are practically unable to absorb water and salts crystallize mainly in pore range from 1 to 10 μm diameter. Pores coarser than 10 μm seem to be produced by salt crystallization. The results are reported below (Tables 2, 3).

Table 2: Porosimetric results. b: brick; s: Istrian Stone

Sample	exposure	Open porosity (%)	Dens. App. (g/cm^3)	Sup. spec. (m^2/g)
IA1 b	rising damp	34.0	1.9	1.1
IA2 b	rising damp	30.0	2.0	9.0
IA8 b	rising damp	41.0	1.8	3.4
IA4 b	sea sparay	28.0	1.7	3.0
IA5 b	sea spray	22.9	2.2	1.1
IA7 s	sea spray	6.9	2.6	1.0

Table 3: Pore size distribution

	Rising damp			Sea spray		
	IA1b	IA2b	IA8b	IA4b	IA5b	IA7s
Pore size (μm)	Cum Vol (%)	Cum Vol (%)	Cum Vol (%)	Cum Vol (%)	Cum Vol (%)	Cum Vol (%)
<0.1	5	30	12	21	12	44
0.1-1	32	53	74	35	37	13
1-10	54	8	8	22	39	5
>10	9	9	6	22	12	38

Brick classified as IA1 was taken from an area strongly deteriorated by the crystallization of soluble salts coming from rising groundwater. The adjacent bricks show strong decay, while investigated samples do not show any evident sign of decay. Porosimetric analysis shows that the sample has more than 80 % of open pores distributed over size ranges of 0.1-1 and 1-10 μm , and therefore should be susceptible to both water absorption and possible salt crystallization.

The analyses of salts also highlight that the total quantity of soluble salts is not more than 1%. The limited decay patterns of this group of bricks is therefore certainly due to its compositional nature and to the firing process which vitrified the external surface, drastically reducing the pore sizes on the outmost surface exposed to higher temperature and generally making the material more resistant to mechanical stress. Such a hypothesis is confirmed by scanning electron microscope (SEM) observations, which emphasized a continuous and homogeneous outer layer, the one that has been vetrified, showing a lower porosity as compared to the internal part of the brick (Figure 6).

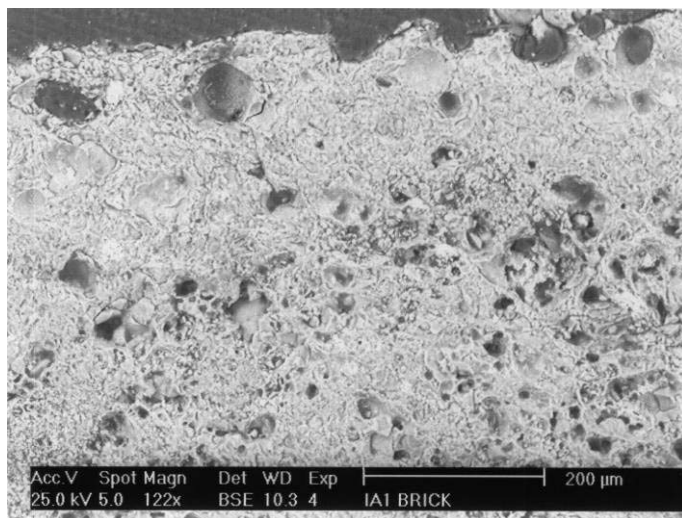


Figure 6: SEM images of IA1 sample external surface

The sample IA8, even if coming from another area, does not show a high percentage of pores with dimensions smaller than 1 μm , and has more than 70 % of pores with dimensions of 0.1-1 μm , a very dangerous range for the possibility of salt crystallization.

The samples IA2, IA4 and IA5, belonging to the same mineralogical group, were taken from an area affected by marine spray and atmospheric pollutants (IA4 and IA5) and by rising ground water (IA2).

The samples IA2 shows more than 80 % of pores with dimensions less than 1 μm (less than 0.1 μm 30 %; 0.1-1 μm 53 %) and 17 % of pores with dimensions coarser than 1 μm , while the samples IA4 and IA5 have more than 70 % of pores size greater than 1 μm . Especially the sample IA5 shows around 40 % of pores with dimensions between 1 and 10 μm . In the sample IA2 the total soluble salts, mostly chlorides, correspond to about 5 %, while in the samples IA4 and IA5 the concentration of total soluble salts, exclusively sulphates, reaches 10.5 and 30.5 % respectively.

The percentage of pores size smaller than 0.1 μm finally results greater in the areas of rising ground water (IA2=30 %) compared to the others (IA4=21 %; IA5=12 %).

The area subjected to marine aerosols and atmospheric pollutants, compared to the one affected by rising ground water, shows a decrease of pores size lower than 0.1 μm and an increase in those with dimensions coarser than 1 μm . This behaviour is directly related to the high amount of soluble salts and on their nature. Sulphates increase pore sizes because, in the Venetian environment, they can withstand more cycles of dissolution, crystallization and hydration, even in a single day.

4 In field tests

4.1 Preparation of the substrate and treatments

In order to consider the different sources of moisture and salts (sea-flooding, rising of groundwater and marine spray) that affect the building, a test area (about 25 m^2) was selected (Figure 7). Before any treatment water absorption measurements in field were performed at different heights at 20, 120, 220, 320, 420 cm from the ground level. Successively the removal of soluble salts was performed by two intensive washings with tap water and two consecutive applications of sepiolite for 24 and 48 hours respectively. To have a good reproducibility of the desalination through the sepiolite, experimental conditions were standardized as much as possible considering the same area of measurements (40x40 cm), weighing the amount of the product before the application (about 320 g on the area of measurements) and considering the same thickness of the poultice layer (about 0.5 cm). In order to evaluate the efficiency of desalination some samples of poultice, removed from the surface, and of washing water were analyzed regarding the soluble salts contents.

Successively five zones 5x0.8 m were selected and the surface was impregnated with white spirit solvent (except for Funcosil IC) and followed by chemical treatments, applied a first time by brush, till the complete saturation. After 6 days a second application was carried-out (except Funcosil IC). The selected products are silicon-based organic compounds that, according to the their physical and chemical properties, can be used for different purposes in the treatment of materials.

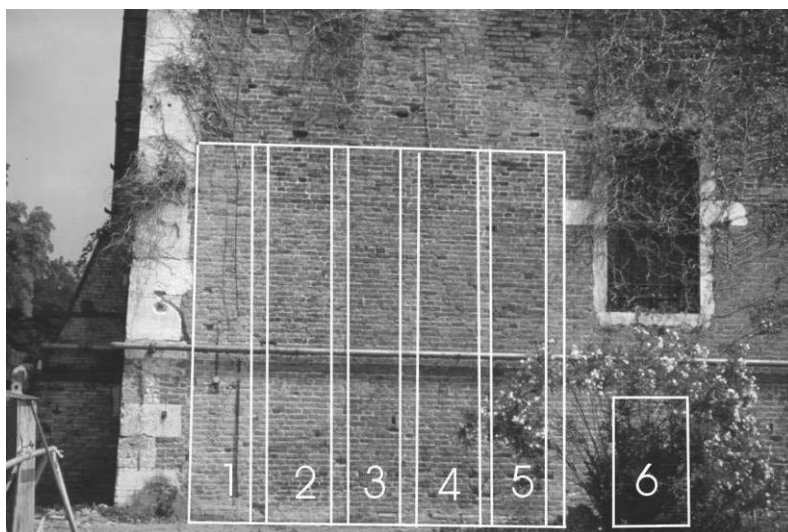


Figure 7: Localization of treated zones on the North side of Torre Alberaria

Treatments and relative applied quantities are described in table 4. Rhoximat HD RC80 was diluite 1:1 in White Spirit. Funcosil IC was applied using a brush in the quantity suggested by the producer. After one and six months from the application, water absorption measurements were repeated at the same heights from the ground level, on the treated zones.

Table 4: Tested products and their consumption

commercial name	general category	Composition	Consumption (ml/m ²)
FUNCOSIL IC	water repellent (cream)	alkyl alkoxy silane and siloxane, emulsion in water	250
FUNCOSIL SNL	water repellent (liquid, solvent based)	alkylpolysiloxane, aliphatic hydrocarbons as solvent	775
Wacker VP5035	consolidant (liquid, solvent based)	alkyl alkoxy silane, organic solvent	787
RHOXIMAT HD RC80	water repellent (liquid, solvent based)	ethyl-silicate and poly-methyl-siloxane mixture, organic solvent	625
RHODORSIL RC90	consolidant (liquid, solvent based)	ethyl-silicate and poly-methyl-fenyl- siloxane mixture, organic solvent	600
DYNASYLAN BSM40SKI	water repellent (liquid, solvent based)	monomolecular alkyl alkoxy silane, anhydrous alchool as solvent	790

4.2 Results and discussion

4.2.1 Water absorption measurements in field

In order to verify the effectiveness of the products, low-pressure water absorption measurements, before and after the application of the products, were carried out. Before the treatment bricks located at 20 cm from the ground-level show the lowest amount of water absorbed during the test (around 2.4 ml) while bricks located in the upper part of the tested area (420 cm from the ground-level) show the higher amount (around 13 ml). The evaluation of the product effectiveness is expressed by the Protection Degree ($PD_p\%$), given by the following percentage ratio:

$$PD_p \% = (AD_{nt} - AD_t) / AD_{nt} \cdot 100$$

where:

AD_{nt} = Absorption Degree before the treatment;

AD_t = Absorption Degree after the treatment.

and:

$$AD = (Q_{tf} - Q_{t5}) / S \quad (\text{ml/cm}^2)$$

where:

Q_{tf} = amount of water absorbed at the end of the test ($t_f=30$ min.) in ml.

Q_t = amount of water absorbed after 5 minutes from the start of the test ($t_5=5$ min.) in ml;

S = contact area between the pipe and the brick (cm^2).

The $PD_p\%$ was calculated after 1 and 6 months from the application of the products. Data obtained comparing the results obtained before and after treatment, allow us to establish that one month after the application the $PD_p\%$ is over 80% for all the tested products (Figure 8), but six months after the application, this parameter is still so high only for Funcosil IC and Dynasytan BSM 40SKI (table 5).

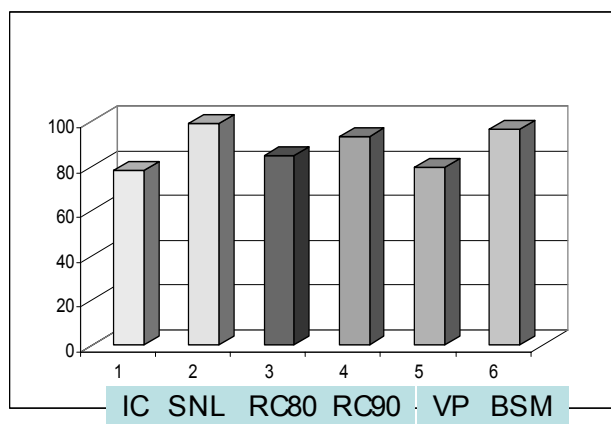


Figure 8: PD_p % after one month from the application

Table 5: PD_p % for Fungosil IC and Dynasylan BSM 40 SKI after 1 and 6 months from the application

PD _p %	Fungosil IC	Dynasylan BSM40SKI
1 month	99	96
6 months	96	100

4.2.2 Scanning electron microscopy analyses

In order to determine the penetration and the distribution of the applied products inside stone capillaries, and the effects of possible interactions of products with soluble salts, some scales of treated bricks have been investigated by means of scanning electron microscopy (SEM) and X ray mapping of marker elements. The selection of marker elements and related products are reported in table 6.

Table 6: Marker elements used for X ray mapping as representative of the substrate, the applied products and the soluble salts

Investigated element	Marker for
Ca	CaCO ₃ , carbonate substrate
Si	Silicon-based products, Silicatic/silicoaluminate
Na, Cl	NaCl, salt contaminant
Al-Fe-K/Mg	Silicatic/silicoaluminate constituent phases of brick
S	Sulphates salts

Morphological observations and X-ray maps performed either on the surface and on cross section of treated samples show different behaviour according to the diverse applied products. The product Funcosil IC forms a surface coating, maximum thickness 10 μm , by deposition of silica gel (Figure 9). The product is visible on pores with average diameter size lower than 1 μm . Sulphates appear to be solubilised after product application and re-precipitated as submicron crystals in the whole pore-network. Some round-shaped cavities are widespread distributed on fresh sulphate crust and distributions of chlorides and IC are superimposable on it.

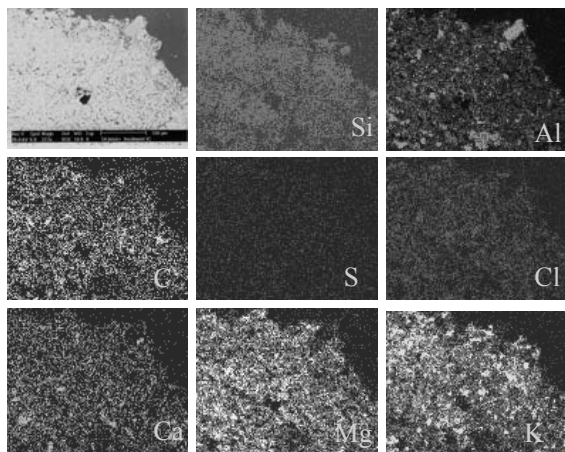


Figure 9: FUNCOSIL IC - BSE image on outmost surface of sample and X-ray maps of the elements

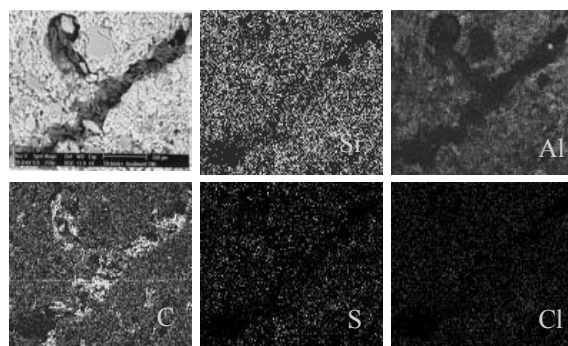


Figure 10: FUNCOSIL SN-BSE image on a crack of sample and X-ray maps of the elements

Funcosil SNL forms a superficial film with a maximum thickness of 150 μm . The product does not penetrate on pores smaller than about 1 μm of diameter and, in coarser pores ($d > 20 \mu\text{m}$), it settles as filament-like aggregates, not as an adherent coating to the substrate. Salts are almost absent (Figure 10). In the sample treated with Rhoximat HD RC 80 it is quite evident a superficial coating, with a maximum thickness of 8-10 μm . The minimum visible pore-size reached by the product is 20 μm and in coarser pores the polymer forms a wide network of organic filaments. Salts are almost absent inside the investigated sample (Figure 11). Rhodorsil RC90 settles as a 20 μm -thick coating and it also migrate inside the pore network up filling pores with dimension higher than about 1 μm . In coarser pores it forms a superficial coating ($\sim 10 \mu\text{m}$ thick) that is often detached from the pore walls, especially on those with an higher salts content (Figure 12). Wacker VP5035 form a superficial film, locally detached, with a maximum thickness is 10 μm . The product reaches pores lower than 1 μm in size and penetrates into the salts crystals (Figure 13). SEM observations of samples treated with Dynasylan BSM 40SKI reveal the presence of a superficial film of product 40 μm thick. The visible pore-size reached is higher than 10 μm , but the treatment has not a homogeneous distribution inside the capillaries. In this case salts are almost absent (Figure 14).

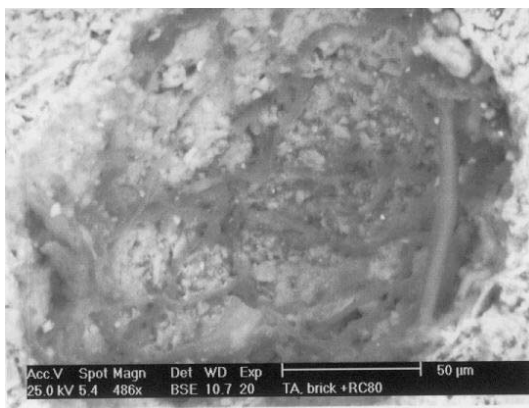


Figure 11: RHOXIMAT HD RC80 - BSE image on a pore containing a network of polymer filaments inside

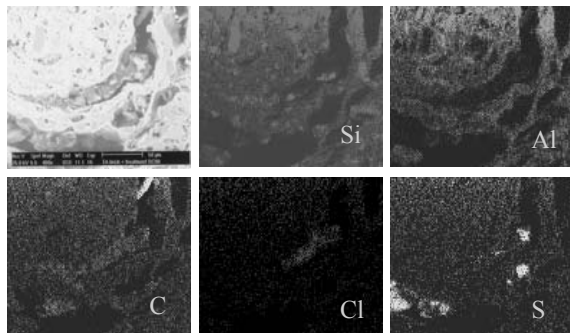


Figure 12: RHODORSIL RC90 – BSE image on some cracks of sample and X-ray maps of the elements

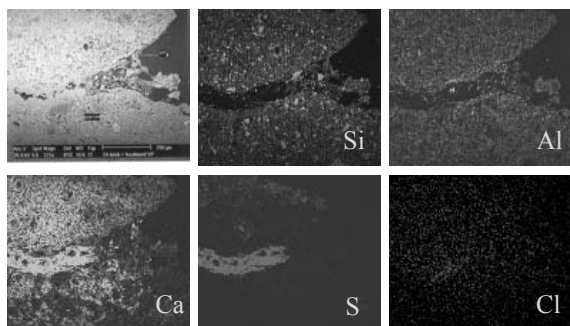


Figure 13: WACKER VP5035 – BSE image on a crack of the sample and X-ray maps of the elements

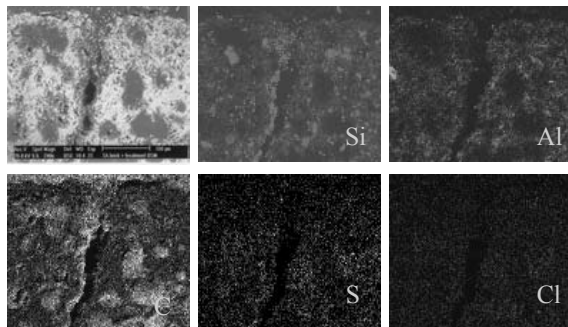


Figure 14: DYNASYLAN BSM40SKI- BSE image on a crack of the sample and X ray maps of the elements

5 Conclusions

Analyses performed for the characterization of the building materials and decay products show a correlation between soluble salts and decay patterns on Torre Alberaria wall masonry. This relationship depends on various factors: the composition of building materials, the nature and quantity of soluble salts, the geographical position of the building and the exposure to environmental phenomena. On the surface chlorides show two peak concentrations at 50 and 250 cm, showing a larger content of salts in correspondence to the evaporation line of high tide water (around 50 cm), and the one presumably "original" from rising ground water (around 250 cm: in this case the salts migrate horizontally from the original wall towards the surface).

Torre Alberaria was chosen to verify the capability of some silicon-based organic compound products to prevent the liquid water absorption and to study their behaviour in the presence of a salt-contaminated substrate. These aims were reached by means of low-pressure water absorption measurements and SEM observations of treated samples collected on the building. Comparing the data obtained before and after treatments, results of in-situ experiments show that at six months from the application only Funcosil IC and Dynasytan BSM40SKI were able to stop the water absorption. In fact at that time the Protection Degree ($PD_p\%$) calculated for these products was over 80%.

SEM observations show that the preliminary washing of the test-area, carried out before applications, strongly reduced the salt content on the wall. It can be seen also that all applied products form a surface coating of variable thickness on the substrate. Funcosil IC gives rise to a superficial deposition of amorphous silica after treatment and it has a solvent effect on soluble salts reducing the dimensions of recrystallised salts. Rhodorsil RC90, Dynasytan BSM40SKI and Wacker VP5035 form an adherent film on pore walls while Funcosil SNL settles as fine elongated aggregates. Furthermore bricks treated with RC90 show a detachment of the coating due to salt crystallization, making its use inappropriate and ineffective on salt loaded substrates. However, to verify the real behaviour of the treatments, measurements should be repeated at least after one year from the application, when the wall should have reached a new equilibrium.

Finally it is useful to stress the necessity of a preliminary desalination of the substrate before the application of a water repellent and consolidation treatment: this operation is crucial for any successful intervention of restoration.

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