Salt Weathering of Masonry Walls The Venice Experience

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Synopsis: All the buildings in Venice insist on foundation immersed in sea water and then are permanently exposed to the capillary rise of salty water containing sodium, chloride and sulfate as main ions. Moreover, due to the closeness of the most important area of chemical industries in Italy, the buildings in Venice are also exposed to the effect of rainfalls containing sulfuric acid. Therefore, the materials of these buildings are between two very dangerous sources of attack one from the earth, the other from the sky, and both related, to some extent, to the action of salts. Capillary rise of sea water from the foundation produces two different types of distress. First, a chemical attack related to sulfate ions occurs, with formation of ettringite and/or thaumasite, which causes cracking and spalling of the rendering mortar. Second, a physical attack related to crystallization of salts (mainly NaCl) within bricks and mortars causes efflorescence and mainly subflorescence deteriorating effects. The prevention measures to avoid these distresses are based on chemical or mechanical barriers against the capillary rise.

Keywords: capillary rise, efflorescence, ettringite, salt crystallization, salt weathering, sodium chloride, sodium sulfate, sub-florescence, thaumasite.
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INTRODUCTION

Most of the historic buildings and monuments in Venice insist on foundations fully immersed under seawater. Due to capillary rise, seawater can permanently or discontinuously wet these structures up to 1 to 3 m high from the ground level. Due to presence of ions present in seawater (such as Na\(^+\), Mg\(^{2+}\), Cl\(^-\), SO\(_4\)^{2-}\), etc.), chemical and/or physical phenomena can occur which cause distresses in bricks, stones and mortars of the involved structures\(^{(1, 2)}\).

In many cases it is not easy to distinguish the specific phenomenon responsible for the distress for the following reasons:

- at given environmental conditions, the prevalent type of distress depends on the quality of the material exposed to the attack; for instance, the chemical composition for a mortar, the porosity for a stone or the presence of contaminating salts for a brick can significantly affect the type and the degree of the distressing mechanism;

- for a given material, the type and the degree of the distress can change as a function of relative humidity, temperature and windy conditions of the environment;

- the coexistence of other potential distressing mechanisms – such as the acid rain typically present in the industrial area close to Venice – can overlap and mask the effect produced by the salts raised by seawater capillary rise.

The purpose of the present paper is to examine the specific contribution of the salt weathering effect on the distress of materials in Venice as different from other mechanisms based on chemical reactions responsible for the distress.
EXPERIMENTAL TECHNIQUES

The work was based on field inquiries and laboratory investigations including X-ray diffraction (XRD) analysis, differential-thermal analysis (DTA), thermogravimetric (TG) analysis, Scanning Electron Microscopy (SEM), chemical analysis by EDAX, and porosity determinations on small samples taken from sound and distressed structures.

RESULTS AND DISCUSSION

Figure 1 schematically shows two typical situations both related to the capillary rise of sea water in masonry walls, followed by drying in two different unsaturated environments: one occurs in a relatively dry and calm air with deposition of crystallized salt on the skin of the plaster (Fig. 1A); the other occurs in a drier and locally very windy air which accelerates the water evaporation even inside the wall under the skin so that the salt deposition occurs within the layer with subsequent detachment of the plaster (Fig. 1B): these two phenomena are known as “efflorescence” (Fig. 1A) and “sub-florescence” (Fig. 1/B) respectively.

Figure 2 shows a typical efflorescence defect with deteriorating effect for the aesthetics of the surface of the wall but without any serious damage for the mechanical consistency, of the plaster. Chemical and XRD analysis indicate that NaCl is the prevalent component of the white stain with minor amounts of other salts. Sometimes the efflorescent stain disappears after a strong and prolonged rain due to the great water solubility of the salts present in the efflorescence. If these salts come from sea water, the efflorescence appears again some time after the rain. If the efflorescence disappears definitely after one or more rainy events, then it means that the salts on the surface of the wall – generally based on sodium sulfate – were caused by some source such as sulfate-contaminated bricks, which is exhausted after some wetting-drying cycles related to rainy and sunny days.

Figure 3 shows a typical subflorescence defect with a more serious damaging effect which causes cracking and detachment of the red-colored lime-pozzolan mortar for the out pushing pressure produced by the crystallization of NaCl just under the mortar itself.

The prevalence of defects based on either subflorescence or efflorescence depends not only on the environmental conditions favoring more or less the water drying from the wall, but even on the porosity of the plaster mortar: in general porous mortars favor more efflorescence rather than subflorescence defects.

* In Venice has been widely used the powder of crushed brick as artificial pozzolan. The Romans used it to replace natural volcanic pozzolan where it was not available as it was near Rome.
The above illustrated defects, both based on physical events related to capillary rise and water evaporation, not always appear so distinctly since other potential distresses, related to chemical mechanisms, can also occur. In the case shown in Fig. 4 the expansion, caused by the ettringite formation, was responsible for the detachment of the cement rendering mortar. The sulfate needed for the ettringite formation was present as impurity in the bricks and reacted with Ca(OH)$_2$ and the C-A-H phase of the cement rendering mortar.

$$\text{SO}_4^{2-} + \text{Ca(OH)}_2 + \text{C-A-H} \rightarrow \text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot \text{H}_3\text{O} \ [1]$$

On the other hand, the damaging effect shown in Fig. 4 cannot be related to some physical effects such as those shown in Figures 2-3: as a matter of fact the sea water capillary rise and the potential crystallization of NaCl were excluded due to the “cutting” of the wall followed by the “insertion” of an impermeable barrier (a lead-plate in the past time or a plastic more flexible sheeting according to the modern technique). This barrier against the sea water capillary rise very popular since the past time in the historic buildings of the Republic of Venice.

Figure 5 shows two adjacent buildings: that on the right does not show any damaging effect because it was dried according to the above “cutting-inserting” technique and so sea water couldn’t rise along the wall; the cementitious rendering mortar of the building on the left hand was severely damaged for two overlapping mechanisms: the physical effect due to the NaCl crystallization and the chemical one producing a destroying effect, related to the thaumasite formation due to the presence of sulfate in the bricks and the C-A-H, C-S-H, CaCO$_3$ of the cementitious mortar:

$$\text{SO}_4^{2-} + \text{C-A-H} + \text{C-S-H} + \text{CaCO}_3 \rightarrow \text{CaCO}_3\cdot\text{CaSiO}_3\cdot\text{CaSO}_4\cdot15\text{H}_2\text{O} \ [2]$$

Specially in the local area where the wall is not directly exposed to sun, the temperature as low as 0-10°C for long period of the winter and authors seasons and the high relative humidity can favor the thaumasite formation in the rendering mortar besides salt crystallization between wall and mortar.

Through the XRD analysis, the presence of sulfate was detected in the bricks of the two adjacent buildings of Fig. 5; however in the dry building on the right, neither the thaumasite formation according to the reaction [2], nor the NaCl crystallization, due to the sea water capillary rise, could occur for the absence of any barrier against the capillary rise of sea water.

The last example of deterioration, related again to a complex mechanism, is that presented in Fig. 6 which shows a thick and impermeable cementitious mortar (about 2m high from the ground level) attached to the wall of a historic building to protect it from the penetration of sea water of the high tide.

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*The destroying effect, much more severe than that related to ettringite formation [1] is due to the removal of C-S-H responsible for the strength of the cement paste.*
The wall was permanently wet for about 2m high from the ground level due to the sea water capillary rise, whereas the cement mortar became saturated in the occasion of the first high tide. Then, due to the swelling, there was a restrained expansion of the mortar due to the bond to the wall, which caused the bending of the mortar (Fig. 7). However, some crystallization of NaCl, found in the space between wall and mortar, could contribute to the detachment of the rendering mortar from the wall.

A recent and effective technique against the capillary rise is based on injections of hydrophobic chemicals, as for instance syloxane, carried out just below the foundation level of the wall so that salts of the sea water are blocked in a humid area and then they cannot crystallize.

CONCLUSIONS

The damage of historic buildings and monuments in Venice is strongly related to the capillary rise of the sea water. However, the acid rain due to the SO₃ emission from industrial areas – not taken into account in the present paper – gives an additional contribution to the deterioration of the historical buildings in Venice.

In the present paper some case histories were examined to show typical damages related to the salt weathering producing efflorescences and sub-efflorescences, and to the formation of ettringite or thaumasite accompanying the salt crystallization.

REFERENCES

Fig. 1 – Efflorescence and sub-efflorescence in masonry walls embedded in wet soils and exposed to dry.

Fig. 2 – Typical efflorescence defect caused by NaCl crystallization on the masonry wall in Venice.
Fig. 3 – Typical subflorescence damage due to the detachement of the rendering mortar.

Fig. 4 – Detachment of a cementitious rendering mortar due to ettringite formation according to equation [1] for the presence of $\text{SO}_4^-$ in the bricks of the masonry wall.
Fig. 5 – Severe damage of the rendering mortar (on the left) due to NaCl crystallization and thaumasite formation according to equation [2], both caused by capillary rise of sea water in Venice. No damage in the wall on the right for the barrier against capillary rise.

Fig. 6 – Cementitious mortar on the wall of a building in Venice to protect it from the sea water during the high side.
Fig. 7 – The mortar shown in Fig. 6 completely detached from the wall due to restrained expansion related to swelling and NaCl crystallization.