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Thaumasite: evidence for incorrect intervention in masonry restoration

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Abstract

Thaumasite, as well as ettringite, are compounds which are increasingly found as deterioration products of cementitious materials subjected to sulfate attack. Thaumasite, and especially ettringite, have been abundantly reported in relation to concrete deterioration as well as, more recently, to the deterioration of cementitious mortars for masonry and for plasters. In particular, the problem appears serious in the field of repair of historical buildings, where the cementitious mortar can easily deteriorate just because of the formation of ettringite and thaumasite. However, although thaumasite is responsible for deterioration, in most cases, it may not be detected since it can be partially or almost completely removed by atmospheric agents.

Many causes can be responsible for the presence of sulfates in masonry. At the same time, mortar and plaster are, in most cases, sources of calcium carbonate. Moreover, masonry is typically a porous material, which can be easily permeated by water, either rising groundwater or falling rainwater. Therefore, when cement based materials, which are in turn sources of calcium aluminates and calcium silicates, are used as binders, all of the ingredients necessary to cause thaumasite formation are present. Consequently, a compatibility issue emerges, which if not kept into proper account, will lead sooner or later to ineffective intervention.
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1. Introduction

By now it is widely accepted and documented [1–5] that one of the most considerable causes of mortar deterioration when employed in masonry either as bricks jointing mortar or rendering mortar for plaster, is related to sulfate salts, often present in the masonry itself. Indeed, if masonry containing sulfate salts is restored by using mortars based on hydraulic binders the risk of failure is well known [1,4,5].

The negative effect is due to the reaction occurring in the presence of humidity, of sulfates contained in the masonry with calcium aluminate hydrates contained in hydraulic mortars to produce ettringite ($C_3A\,Cs_3\,H_{32}$) or with calcium silicate hydrates of the same mortars to produce thaumasite ($Cc\,Cs\,CS\,H_{14.5}$). In the case of plasters, ettringite formation is accompanied by mortar swelling, spalling and detaching. On the contrary, when the employment of hydraulic mortars leads to the formation of thaumasite, the plaster deterioration reveals itself by means of a progressive removal of mortar due to washing out by rainwater [4], because of its alteration into a pulp in wet and cold climates. The same phenomena can of course also appear before restoration owing to the employment of pozzolanic mortars, which are hydraulic even if not necessarily cementitious.

The presence of sulfate in masonry may come from direct employment in the form of gypsum either alone or in addition to lime, as binder in original mortars (in particular for rendering) or in mortars used for later interventions of either maintenance or restoration. On the other hand, it is well known that bricks too can commonly contain an appreciable amount of hydrosoluble sulfates [6,7], which can be carried from water in wet masonry. The presence of sulfates in the masonry can also come indirectly from the environment, owing to capillary rise of water containing sulfates from foundations or to wind transportation in marine environments. Nevertheless, especially due to the increasingly severe climatic conditions in city centres, a further kind of sulfate source in masonry cannot be neglected. This originates from heterogeneous oxidation [8,9] in liquid

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phase of sulfur dioxide contained in emissions from combustion of both light and fuel oils. On the other hand, owing to the high porosity of rendering mortars and their nature, mainly based on calcium carbonate, this mechanism of environmental sulfation cannot be excluded in advance, and indeed this hypothesis has already been suggested [10].

The above described evidence has lead to a growing awareness in the compatibility of materials employed for restoration, in order to avoid undesirable damage from the restoring intervention itself. Moreover, a properly planned intervention requires a careful preliminary diagnostic survey [11], so that deterioration mechanisms, if any, and compatibility issues can be pointed out.

In any case, although ettringite and thaumasite are increasingly found among the deterioration products of cementitious mortars used for masonry and for plaster of historical buildings, it is nevertheless difficult to evaluate with the most available method, X-ray diffraction, the presence of these compounds, because their characteristic lines are modified in intensity and/or position by environmental thermo-hygrometric variations [12]. Ettringite is reversibly affected by the decrease in relative humidity and increase in temperature. Thaumasite is mainly affected by temperature increases and needs a long time for its structural recovery. Therefore, a correct diagnosis is very difficult when thaumasite has been decomposed by thermal effects.

2. Experimental survey

Samples of damaged plasters were examined from two buildings located in the same ancient district of the Ancona harbour, but different for feature, age, historical interest and exposure to wind transportation in the marine environment.

Fig. 1. Deterioration of the rendering mortar caused by ettringite (a) and thaumasite (b) formation in a building located in the historical centre of Ancona.

The building shown in Fig. 1 is located in the historical centre of Ancona, behind the harbour, not directly exposed to marine action. It was built during 17–18th centuries but it has no particular relevance from an historical and architectural point of view. Just for this reason, it was an excellent laboratory of field research, particularly interesting to study both materials and building techniques currently employed there at that time, and to study structural and material changes undergone during later interventions of either maintenance or restoration. The building shown in Fig. 2, the Vanvitelli's Mole, is on the contrary a monumental building erected in the 18th century and it is located inside the Ancona harbour. Its foundations are immersed in the sea and it is directly exposed to the action of sea-water.

In relation to aggressive exposure, the former building, in spite of repeated interventions for transformation and maintenance, does not show particular deterioration. This is due to the employment of gypsum as a binder, which was mainly used in internal mortars during reconstruction after the damages of the second world war, and to the particular capillary rise of water from foundations. However, the external rendering mortar exhibits severe deterioration, apparently attributable to ettringite and thaumasite formation from a morphological point of view, since sharply detached mortar (Fig. 1a) is observable close to smooth removal of the same mortar (Fig. 1b), which is evidence of these products.

In contrast, the Vanvitelli's Mole certainly appears more exposed to the deteriorating action of marine environment as a whole, particularly due to the remarkable capillary rise of sea-water through its masonry walls. As a matter of fact, in this case severe deterioration in the form of widespread hollowed joints and detached rendering mortar is observable.

In this paper, the results are reported in relation to examinations carried out on both jointing and rendering mortars of the two buildings in order to single out likely deterioration mechanisms. Examinations were carried out by X-ray diffraction analysis on samples removed at different depths from the surface in order to establish the

Fig. 2. The Vanvitelli's Mole in Ancona.

binder nature and, particularly, to determine the gypsum, ettringite and thaumasite contents in the different samples. In fact, X-ray diffraction analysis has always been considered to be a powerful tool to detect the crystalline components present in cementitious materials. However, this technique becomes ineffective if the amount of minor components is below a certain threshold, as often occurs when searching for ettringite and thaumasite in the deterioration products. In addition, the situation is complicated by the overlap of the main XRD lines belonging to both these products. Because of the above mentioned problems, an advanced technique was applied to data elaboration in order to enhance even very weak XRD peaks, as suggested in a previous work [13].

3. Results and discussion

The results obtained from X-ray diffraction analysis on samples taken from the building shown in Fig. 1 allowed concentration profiles of gypsum and ettringite to be drawn along the cross section of the wall thickness, reported in Fig. 3. The presence of gypsum in the samples of jointing mortar removed from inside just behind the plaster, made of gypsum and sand, can be attributed to migration phenomena supported by thermo-hygrometric changes. On the contrary, the presence of gypsum together with ettringite in the samples removed from the outside of the masonry wall is evidence of the hydraulic nature of the binder used to prepare the rendering mortar. This is valid for both the originally employed hydraulic lime or lime–pozzolan blend, or even for the cement used during later and more recent interventions of plaster resumption and maintenance. On the other hand, the total absence of thaumasite in these samples could mean that, if formed, it was washed out by atmospheric agents. Indeed, its formation could not be excluded just because of the presence of ettringite and its transformation into a pulp could also not be excluded because of usual winter climate conditions in the area.

Since no significant capillary rise of water was observed in the masonry, the presence of ettringite in the external plaster and its related deterioration could be attributed to sulfate attack from the environment.

Instead, X-ray diffraction analysis carried out on samples of jointing mortar removed from masonry walls of the Vanvitelli's Mole, reported in Fig. 4, showed that

- the interior jointing mortar contained quartz and calcite, typical constituents of mortar made of lime and sand;
- the external jointing mortar (corresponding to the joints on the facade surface) contained gypsum and calcite, whereas the absence of quartz in it could mean that, during construction or even old repair works, sand was replaced by pozzolan in order to ensure durability of external joints;
- the external jointing cement mortar (so called because of the presence in it of anhydrous cement constituents), believed to be applied during recent interventions of repair and maintenance, contained calcite, quartz, ettringite and thaumasite.

Moreover, gypsum, ettringite and thaumasite were also found in samples of deteriorated plaster (Fig. 5), almost certainly made with cement since it was detected in the rendering mortar. Again, the deterioration origin could only be an aggressive environment. Without neglecting marine spray, which has always accompanied the life of the building, deterioration has rapidly increased in the last decades, corresponding to an increasing content of sulfur dioxide in the atmosphere. This environmental attack is detrimental for cement

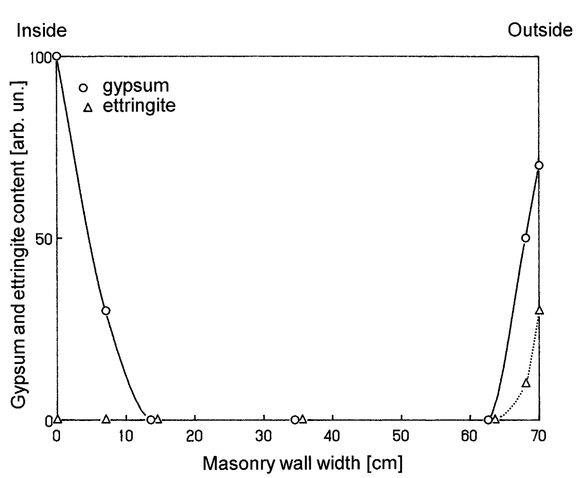

Fig. 3. Gypsum and ettringite content profile through cross section of masonry walls of the building shown in Fig. 1.

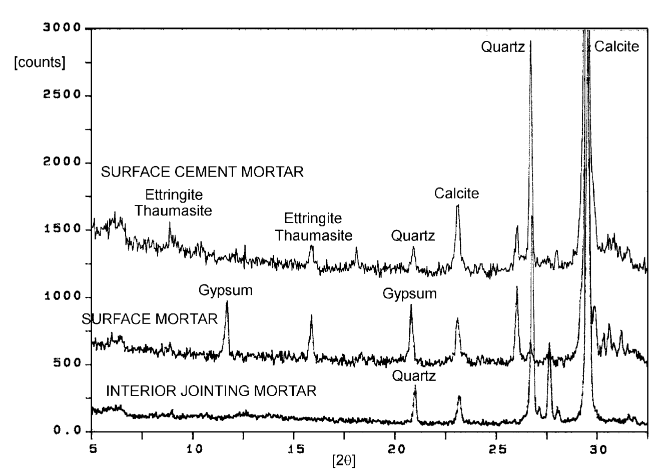

Fig. 4. X-ray diffraction results obtained on jointing mortars picked up from masonry walls of the Vanvitelli's Mole.

Fig. 5. Deterioration of rendering mortar of the Vanvitelli's Mole.

mortars, since calcite sulfation provides the source of gypsum, which is necessary for subsequent ettringite and thaumasite formation [3–5].

4. Conclusions

Samples of rendering and jointing mortar, removed from two buildings located in the same area but differently exposed to various sulfate sources, were examined. Deterioration, detected only for rendering and surface jointing mortars through gypsum, ettringite and thaumasite formation, appeared quite similar for both buildings in spite of different exposure to sulfate aggression. This evidence makes the environmental sulfation mechanism the most likely one responsible for deterioration.

The presence of ettringite and thaumasite in the deterioration products means that mortars were made with hydraulic binders, either original lime–pozzolan or cement used during later interventions, not compatible with sulfate generated by the above mentioned environmental attack. Therefore, thaumasite, as well as ettringite, are evidence of incorrect intervention.

As a concluding remark, when repair or restoration interventions are to be made on masonry walls in which gypsum, ettringite and thaumasite are detected, a sulfate resistant binder should be used and precautions should be adopted in order to block water permeation of masonry.

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