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Thaumasite as decay product of cement mortar in brick masonry of a church near Venice

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Abstract

Thaumasite has been recognized as constituent of salt efflorescences occurring within the cementitious mortar connecting the brick framework. It gives rise to swelling fissures and scaly detachments; furthermore, to heaving, curving and spalling of the perimeter walls.

The sand aggregate of the mortar contains carbonates (calcite 25–40%, dolomite 20–35% and aragonite 5–20%). The bricks rarely contain negligible amounts of gypsum, whereas, together with Mg–calcite and dolomite, it constitutes very thin patinas covering some bricks exposed to south: probably, such patinas originated by precipitation from solution percolating through the joint mortar.

It is noteworthy that thaumasite efflorescences are mainly located at the north-side of the perimeter masonry, and their amount is higher (up to 30%) on the internal walls where lack of direct sun-radiation, narrow range of temperature changes and dew-condensation conditions actually keep up a rather constant and relatively high room moisture ratio, and low temperature.

The most probable source of pollutants should be discharges (exhaust gases, as sulphur oxides) from the large petrol-chemistry industrial area located in the neighbourhood of Mestre town, inside the Venice lagoon.

Morphological features and air drying behaviour of the thaumasite crystals, as observed by Environmental-SEM, indicate that their growth took place in conditions far from equilibrium, e.g. at different supersaturation values.

Keywords: Thaumasite attack; Above-ground construction; Brick masonry; Mortar carbonate-aggregate; Industrial pollution source

1. Introduction

Sulphate attack on cement-based construction materials is one of the most frequent and damaging phenomenon evidenced through expansion, cracking, decomposition, etc. of the resulting products of cement hydration. Among the processes that can generate a decrease in mechanical strength, the formation of gypsum, monosulphoaluminate, sodium sulphate and ettringite have been recognized for many years. However, during the last decade, cases of a new form of sulfate attack (the thaumasite form) have been discovered in buried concretes and/or mortars where significant damage of the matrix occurs as a consequence of the replacement of cement hydrates by thaumasite.

Thaumasite is a complex calcium salt, for which most of the authors acknowledge the stoichiometrical formula $CaO \cdot SiO_2 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$.

Formation of thaumasite in cements and its negative effects on mortars and concretes has not been well enough studied yet. A critical review [1] of the state of the art on thaumasite formation has been drawn up with the main objective to stressing the aspects that consider its formation in mortars and Portland-cement concretes, and also the effect its formation has on their durability.

Investigative studies had shown that the thaumasite form of sulfate attack (TSA) is different from the conventional form of sulfate attack, as TSA requires a source of carbonate and cold wet conditions for the reaction to occur.

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The expansive ettringite formation can be prevented and consequently its destructive effect avoided. In the case of thaumasite this is not possible, since the mechanism of its formation is not well known.

The UK's "Thaumasite Expert Group", after examining the published and on-going research data, has prepared a report [2] on diagnosis, risks, remedial works guidance and interim recommendations to minimize the risk of TSA for both existing structures as well as for new construction.

The present paper presents the results of a study carried out on thaumasite efflorescences developed on/within mortars used for the brickwall-framework of a church constructed in the 1970s (locality of Annone Veneto, about 60 km N–E of Venice, northern Italy), showing fissures along the brick–mortar joints and scaly detachments of the bricks' surfaces, which are causing heaving, curving and spalling of the wall masonry.

The aim was to elucidate the causes of the decay processes, i.e. the influence of mortar aggregate composition and environmental conditions on thaumasite formation.

2. Setting, materials and methods

The parish church of Annone Veneto/VE, is a monumental basilica devoted to St. Victor Martyr (San Vittore Martire) by a legacy delivered on the occasion of the Vaticano II Council; it is serving a large catholic communion district. Its construction was completed in 1976: Fig. 1 shows external and internal views of the building which is composed of the Main Amphitheatre (m 28×43), the Chapel and underlying Crypt; besides, there are the Sacristy and small service rooms.

The bricks used for the wall-framework are "semi-gres" products, whereas the mortar is a mix of sand and cement. The sand aggregate of the mortar is mainly composed of carbonates in ranging amounts: calcite 25–40%, dolomite 20–35% and aragonite 5–20% (see Table 1); other constituents such as quartz, feldspars and micas are subordinate together with traces of clay minerals. In fact, the used sands come from coastal-marine sediments (coast-line of northern Adriatic Sea), which contain fluvial debris ("Dolomites" region, eastern Alps, as source area) and remnants of mollusk shells [7–10].

Bricks mortars and salt efflorescence were analysed by X-ray diffractometry (XRD, powder specimens), using a Philips PW 1800/10-diffractometer; they have also been examined by Environmental Scanning Electron Microscopy (ESEM), Electroscan Corporation model E-3, at controlled moisture content. The apparatus are respectively set at the Department of Earth Sciences, Laboratory for Clay Research and Archaeometry, Pavia University (Italy), and at the Conservation Institute of the Getty Centre, Los Angeles—USA. The X-ray fluorescence analyses of bricks were courteously performed by prof. L. Leoni (Department of Earth Sciences, Pisa University—Italy).

For analytical methodologies and procedures refer to [1–3] and references listed therein.

The analysed samples have been collected on walls exposed to all geographic directions, both from external and internal sides.

Fig. 1. External and internal views of the church building.

Table 1
Mineralogical composition of <125 μm fraction separated from bulk mortars (XRD evaluation)

	Exposure				
	South	West	North	North	Concentrated by ultrasound
Thaumasite (%)	–	Traces	19	28	35
Gypsum (%)	5	3	–	Traces	2
Calcite (%)	41	32	25	22	23
Dolomite (%)	33	29	21	17	9
Aragonite (%)	6	19	15	12	20
Quartz (%)	15	17	20	21	11

3. Decay aspects of the brickwalls

The brickwall frameworks show several damage aspects (Fig. 2): scaly detachments from the brick surface, fissures, cracks and salt efflorescences. Fissures are concentrating along brick–mortar joints (B, D), whereas cracks cut across the bricks themselves (A). Scaly detachments observable on the external brick surface (A, C), in some instances are accompanied by thin whitish salt efflorescences. The fissures are sometimes located along damaged mortar–brick joints (B) which become detached from each other (D). Heaving and spalling of brickwalls are the result of such decay.

The whitish thaumasite efflorescences are mainly recognizable on the northern side of the building, and they are more abundant on the internal side of the walls (Fig. 3A); they are absent on walls exposed to south (Fig. 3B).

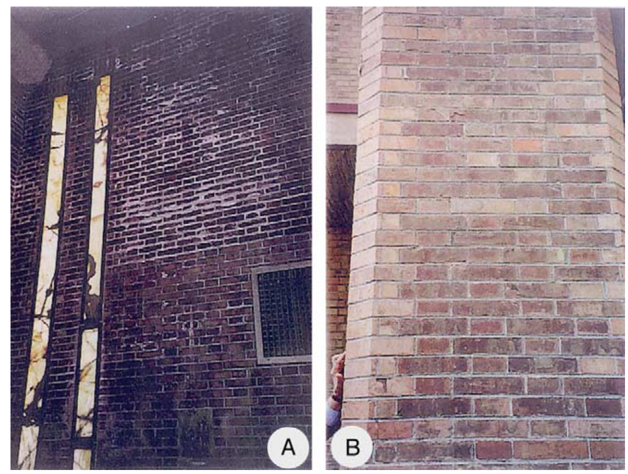

Fig. 3. (A) Thaumasite efflorescences on the internal side of a brickwall exposed to north. (B) External brickwall exposed to south without thaumasite efflorescences.

Fig. 2. Decay aspects of the brickwalls (see text).

4. Analytical results

Mortar bulk samples and whitish efflorescences were analysed by XRD (powder specimens), and examined by ESEM observations.

Mortars contain different amounts of thaumasite (Fig. 4, and Table 1), depending upon the exposure of brickwalls. Thaumasite is more abundant (20–30%) within mortars of brickwalls exposed to the northern side of the perimeter masonry, and its amount is higher

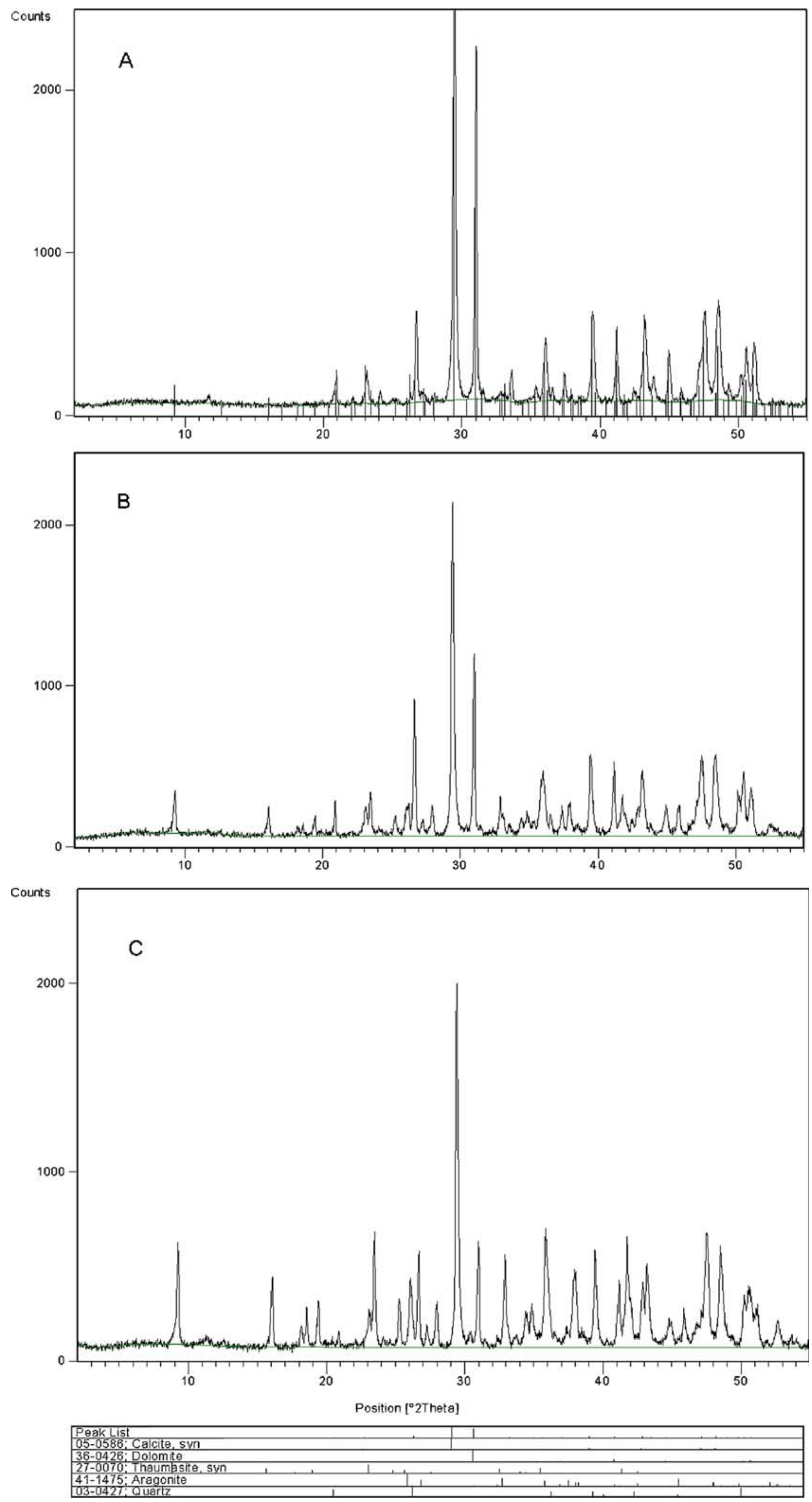

Fig. 4. XRD diffraction traces of <125 μm fraction separated from mortars, collected on south (A) and north (B) exposures of brickwalls; (C) is a further finer concentrate of (B) obtained by ultrasound treatment.

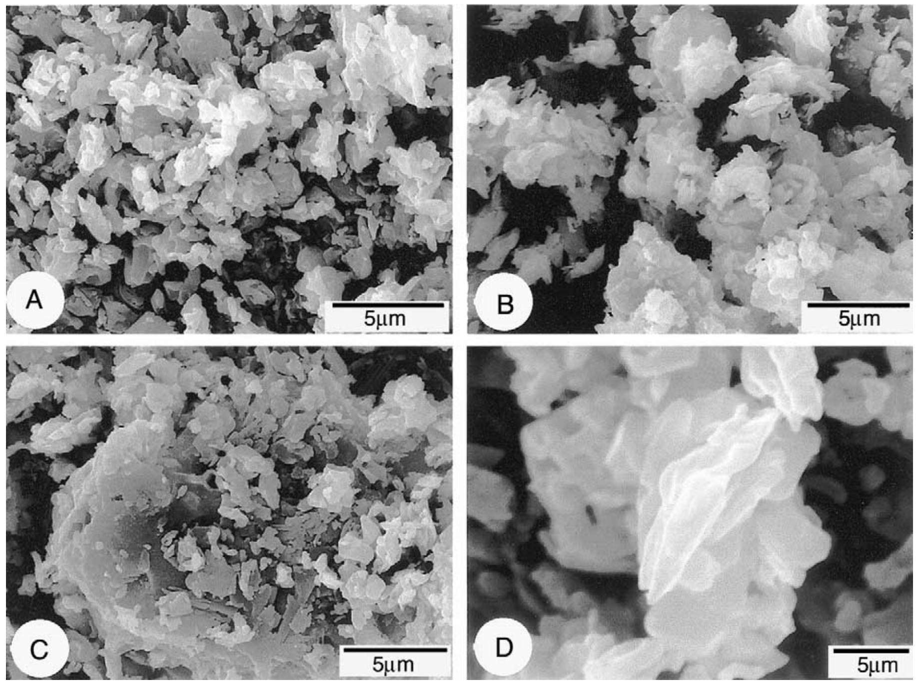

Fig. 5. ESEM observations: (A) moisted specimen; (B) and (C) air-dried specimens; (D) detail of crystal morphology.

on the internal side of the wall (Fig. 3A). Mortars from brickwalls exposed to south are exempt from thaumasite (Fig. 3B), whereas it is scarce on brickwalls exposed to west. Whitish efflorescences are almost pure thaumasite.

Detailed ESEM observations of the thaumasite efflorescences (Fig. 5) have shown the presence of plate-like crystals that aggregate when air-dried. Their sizes range from <1 to 15 μm. Most crystals show wavy surfaces and corroded edges. Crystals with elongated habits and pin-like ends are in lesser amount. Well developed crystals, i.e. showing well formed faces, have rarely been observed in samples air-dried at room temperature.

5. Discussion and conclusion

Visual inspections, XRD analyses and ESEM observations show that the whitish efflorescences located on brick surfaces, within mortar pores and between brick/mortar joints of the masonry walls of the parish church of Annone Veneto/VE (northern Italy) are composed of thaumasite (refer to previous publications listed in [1,2]). This decay by-product is more concentrated (20–30% of the bulk samples) on the walls exposed to north, especially on the internal side where lack of direct sun-radiation, narrow range of temperature changes and dew-condensation conditions actually keep a rather stationary and relatively high room moisture ratio, and low temperature. Noteworthy, the site has cold and humid (foggy) climate during autumn and winter.

These data confirm previous results suggesting that thaumasite formation needs preferably a cold ambient temperature (2–10 °C), although it can be also generated slowly at room temperature or even higher [1,2].

As a general rule it is admitted that thaumasite does not form on the surface of mortars or concretes in direct contact with fog and/or rain water, but it most likely forms behind the surface where the mortar remains saturated with water for longer periods, although there are authors asserting that the formation of thaumasite starts from the surface of the sample.

In some instances, the morphologies of thaumasite crystals observed on the masonry walls of the church of Annone Veneto/VE may indicate that crystal growth took place in conditions far from equilibrium (i.e. at different supersaturation values). Such morphologies and growth pathways resulted in high crystallization pressure which caused damages of the porous mortars and bricks (expansion, detachment and cracking), which caused curving, heaving and spalling of the brickwall frameworks.

Investigations [4–6] concerning the influence of salt nature and crystallization time on the deterioration of porous building materials (mortars and bricks) under different thermo-hygrometric conditions, and the consequent different damage types and mechanisms produced, have attributed the main deterioration factor to the pressure developed during crystal growth. In this context, crystal habits and number of crystal seeds, their growth rate and solubility, the expansion/shrinkage accompanying hydration/dehydration cycling, play important roles.

Table 2
Chemical composition of a representative brick sample

LOI	2.90%
SiO_2	54.48
Al_2O_3	13.22
Fe_2O_3	6.39
CaO	16.15
MgO	3.19
Na_2O	0.92
K_2O	1.81
TiO_2	0.81
MnO	0.07
P_2O_5	0.07

The threshold necessary for the breakdown of a mortar due to TSA probably lies somewhere between 15% and 35% of thaumasite: such values have been detected within the mortars of the brickwalls of the church of Annone Veneto/VE (see Table 1).

It is to be noted that the significant damage of the matrix of concrete or mortar as a consequence of the replacement of cement hydrates by thaumasite (in some instances favoured by pre-existing voids and cracks) is different from the conventional forms of sulphate attack when gypsum and ettringite are formed, as the TSA requires a source of carbonate for the reaction to occur. It is interesting to remark that dolomite is considered more reactive than calcite. In fact, dolomite reciprocally decreases as thaumasite increases (see Fig. 4). The necessary CO_2 can also be derived from the polluted atmosphere as well as the sulphate source. The deterioration is more

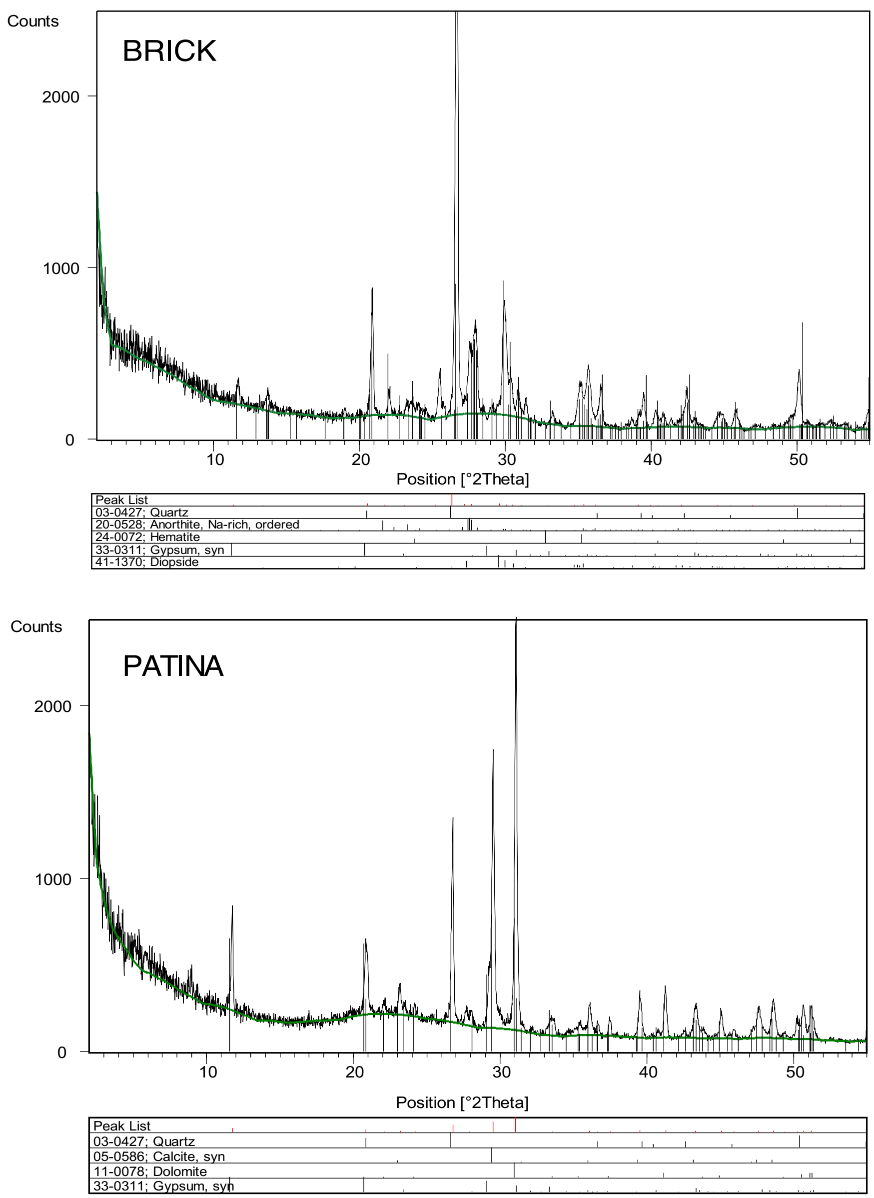

Fig. 6. XRD diffraction traces of a representative brick sample, and of a thin patina covering the brick surface.

rapid when mortar is in contact with water that contains Mg^{2+} ions, as for marine water.

In the case of the brickwalls of the church of Annone Veneto/VE, the mortar inert aggregates are made up of carbonate rich-sand coming from regional river debris or dredged from the coastal-line of the northern Adriatic Sea [7–10].

The effect of alkali-aggregate reaction is also important. Silicon can be derived from cement hydrates and, additionally, can result from the alteration of mica, feldspars and clay minerals present in the sands used as inert aggregate of the mortar.

Bricks from the external southern façade of the church, where thaumasite efflorescences have not been observed, were analysed in order to verify the presence of salts. The chemical composition of a representative sample, determined by X-ray fluorescence, is reported in Table 2.

X-ray diffraction trace (Fig. 6) indicate the presence of a very low amount of gypsum within the bricks itself, whereas higher amounts, together with Mg–calcite and dolomite (these carbonates are also constituting the mortar aggregate grains), are present in thin patinas covering the brick surface. Such kind of patinas seem to be precipitation products from solution percolating through the joint mortar.

Noteworthy the presence of gypsum and absence of thaumasite on brick surfaces at the southern exposure, where temperature ranges and moisture condition are quite different with respect to northern exposure (here thaumasite is the predominant constituent of efflorescences, especially developed on internal walls; its formation is due to the peculiar micro-environmental conditions as already mentioned above).

Actually, the most probable source of pollutants should be the discharges (exhaust gases, as sulphur oxides) from the large petrol-chemistry industrial area located in the neighbourhood of Mestre town, inside the lagoon of Venice.

The TSA needs adoption of approaches suitable to avoiding its occurrence. It has mainly been discovered in buried concrete (foundations, piles, road sub-bases, tunnels, etc.), even constructed with sulfate-resisting cement, specified in accordance with current guidance.

The case of the church of Annone Veneto/VE, where the thaumasite occurs in an above-ground construction, is a peculiar one. Care was paid in selecting appropriate materials for correct repair and rebuilt interventions of the brickwall parts damaged by thaumasite efflorescences, using a mortar made up of a mix of siliceous inert aggregates and a hydraulic binding, thus suitable to avoid sulphate and alkali attack.

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