Mortar deterioration of the masonry walls in historic buildings. A case history: Vanvitelli's Mole in Ancona

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The utilization of data from advanced techniques, such as enhanced pattern treatment of x-ray diffraction analysis, combined with data from historical sources as well as environmental information, has been applied to diagnose the complex deterioration mechanism of a historic construction. A case history is provided dealing with a famous Italian construction in Ancona designed and erected by the Neapolitan architect Luigi Vanvitelli during 1733-1743, where both jointing and rendering" mortars deteriorated very seriously. It has been found that the original lime-pozzolan mortar deteriorated due to physical events (rain water leaching, thermal changes, freezing-thawing, etc.), whereas Portland cement mortars, used to repair damaged walls, deteriorated by chemical sulfate attack.

1. INTRODUCTION

The deterioration of actual structures, in the absence of known and controlled conditions such as those achievable for laboratory specimens, is always due to very complex mechanisms. Various circumstances can take place simultaneously: the materials used may be dissimilar and sometimes unknown; multiple maintenance operations might occur before the diagnosis. Furthermore, for historic buildings the diagnostic problem is much more complicated than for modern concrete structures because of the longer exposure to changeable and unknown environmental (microclimatic and urban) conditions. Finally, for historic buildings, subject to restrictions by public authorities because of their considerable architectural importance, these are additional diagnostic difficulties due to the limited number and amount of collectable samples.

In spite of these difficulties our efforts have been devoted to investigating the deterioration mechanisms of very complex historic buildings, such as that examined in the present work: Vanvitelli's Mole in Ancona. This building (Fig. I) was erected by Luigi Vanvitelli between 1733 and 1743 on an artificial purpose-built island in Ancona harbour. The building was designed to be a pesthouse. In the course of its lifetime, the Mole was subjected to frequent changes in its use $-$ barracks, military hospital, warehouse, sugarworks and tobacco storehouse - continually undergoing alteration works which have significantly distorted the original building: several extensions were put up; two new bridges were

built to link the island to the shore; a railway was laid on the road running within the boundary wall; openings and floor levels were changed; the internal space layout was even irrevocably modified by constructing reinforced concrete frames inside some building units [1].

At present, restorative treatments, based on the results of preliminary investigations, are intended to make up for the consequences of the above-mentioned disregard for the building: the present work is a contribution to this preliminary diagnostic activity.

Fig. 1 A general view of Vanvitelli's Mole in Ancona, Italy.

2. PRELIMINARY DETERIORATION SURVEY

Because of the extensive state of deterioration of both the bricks (Fig. 2) and the mortar (Fig. 3) of the masonry walls, a survey specifically devoted to the materials used in the building has been carried out. The deterioration survey includes sampling the materials (bricks, mortars and efflorescences) for examination using chemical, mineralogical, physical, and mechanical tests. In addition to these laboratory tests, some *in situ* examinations, such as flat jacks, endoscopies and foundation inspection, have been carried out. Finally, all the results of these laboratory and *in situ* tests have been correlated with supplementary information concerning the environment, the climate, the history and the architecture of the building. In the present paper, for reasons of brevity, only the results concerning mortar deterioration will be examined.

3. CAUSES OF DETERIORATION OF MORTARS IN HISTORIC BUILDINGS

It is well known $\lceil 2 \rceil$ that various deterioration mechanisms, due to environment interaction with building materials, can occur, in which water always plays a primary role.

Fig. 2 Deterioration of bricks and jointing mortars.

Fig. 3 Deterioration of rendering mortar.

- (a) physical causes, as in the case of freezing-thawing, leaching out, crystallization of water-soluble salts;
- (b) chemical causes, due to ettringite and/or thaumasite production $\lceil 3 \rceil$ as a result of the reaction between sulfate salts and hydrated calcium silicates or aluminates which are present in mortars based on cement, hydraulic lime or lime-pozzolan; and
- (c) biological causes, as in the case of formation of algae, lichens and fungi. These specific causes have been excluded in the present work.

4. METHODS AND MATERIALS

x-Ray diffraction (XRD) analysis has always been considered to be a powerful tool for detecting the mineralogical crystalline components which are present in cementitious building materials $[4]$. However, this technique has substantial limitations due to the difficulties in detecting the minor components whose amounts are below a certain threshold. In the present work, an advanced XRD technique has been used which is based on a software package (PC-APD Philips Software for Automatic Powder Diffraction), which enables identification even of minor components.

When using the traditional XRD techniques, the chemical products to be analysed in a sample should be present in quantities of several per cent in order to detect the corresponding peaks on the XRD pattern. This means that, in a mortar or concrete, with aggregate/cement ratio by weight of 3:7, it is very difficult to detect the anhydrous mineralogical components of Portland cement even after a few days of hydration. Moreover, the main hydration product of Portland cement (tobermorite, CSH) is nearly amorphous, so that it is very difficult to detect it by XRD. The other main component of a mature cement paste, $Ca(OH)_2$, in general is transformed within a few months into CaCO₃ due to carbonation by $CO₂$ of the air, so that the XRD peak of this final product cannot be distinguished from the XRD calcite peak belonging to limestone aggregate. All these things together mean that it is practically impossible to distinguish a cement mortar from a lime or lime-pozzolan mortar after some months or a few years of curing.

As far as the diagnosis of the material degradation is concerned, even one of the most important and well known mechanisms of attack on cementitious materials $-$ sulfate attack $-$ is hardly ever distinguishable, by the traditional XRD technique, as causing ettringite or thaumasite production, because of the almost identical position of the main XRD peaks belonging to these products which are both responsible for the effects of sulfate attack.

By using the new automatic XRD analysis, it is possible to detect in a mortar sample the Portland cement anhydrous mineralogical components even after many years of curing, as well as to distinguish ettringite from thaumasite very easily even if present only in traces.

Fig. 4 XRD patterns (original, fitted and treated) of an interior jointing mortar with traces of gypsum (G) and large amounts of quartz (Q).

Indeed, through the 'profile fitting' technique the original XRD pattern can be treated in order to enhance very weak peaks belonging to products which may be present even in traces. For instance, Fig. 4 shows the original unmodified XRD pattern and the fitted one as well as the treated one of a lime-pozzolan mortar which contains large amounts of limestone-quartz based sand and only traces of gypsum.

The mortar samples examined in the present paper belong to three different types, schematically represented in Fig. 5: (i) interior jointing mortars (9 samples); (ii) facade jointing mortars (3 samples); and (iii) rendering mortars (5 samples). Consequently, the results are dealt with in three sections.

5. RESULTS AND DISCUSSION

5.1 Interior jointing mortars

Even with the advanced XRD technique, it is very difficult to detect CSH (in the form of an ill-crystallized product corresponding to the 'tobermorite gel' described by Taylor [4]) in the interior jointing mortar samples: this is due to the high percentage $(70-80\%)$ of fine aggregates (quartz and limestone) and to the relatively low amount of cementing material in which CSH would be present. The formation of CSH should be caused by reaction of lime with amorphous silica from a pozzolan:

$$
Ca(OH)2 + SiO2 + H2O \rightarrow CSH
$$
 (1)

This would seem to be a little surprising because,

Fig. 5 Schematic representation of the brick masonry wall (cross-section) to illustrate the terminology.

in the area where the building was erected (Ancona), natural pozzolan was not available. However, there are historical sources [1] which support the hypothesis of pozzolan utilization for Vanvitelli's Mole: according to

these documents a pozzolan freight was transported from the Naples Gulf to Ancona, by boats sailing right round South Italy, just for the artificial island on which Vanvitelli's Mole was subsequently erected. Therefore, the utilization of natural pozzolan for the jointing mortar of the brick masonry walls of this building cannot be excluded, and this would explain the CSH formation in the inside jointing mortars.

Traces of gypsum (Fig. 4) as well as other sulfate salts have been detected by XRD. The amount of gypsum is so small that its presence cannot be ascribed to the utilization of a gypsum-based mortar. Therefore, gypsum must have been formed by water soluble sulfate salts, coming from bricks or sea water capillary rising and reacting with lime:

$$
Ca(OH)_2 + SO_4^{2-} + H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH^-
$$
\n(2)

It has been suggested [2, 3] that thaumasite could be produced by reaction of CSH, formed in lime-pozzotan mortar, with gypsum. In the samples of the interior jointing mortars, neither thaumasite nor ettringite has been detected, even by using the advanced XRD technique. Perhaps the amounts of CSH and gypsum are too small to produce detectable amounts of thaumasite. Therefore, deterioration of the interior jointing mortars, resulting in disintegrated surface joints (Fig. 5) should be ascribed to mechanisms different from chemical reactions producing ettringite and/or thaumasite. Physical effects such as freezing-thawing, salts crystallization,

or water leaching, appear to be responsible for the deterioration of these mortars.

5.2 Facade jointing mortars

Facade jointing mortars have been examined as a potentially different material from the interior jointing mortar (Fig. 5), mainly because of different colour and/or appearance. The XRD analysis has confirmed this hypothesis. Indeed traces of C₃S, C₂S, C₃A and C₄AF $(C = CaO, S = SiO₂, A = Al₂O₃)$ have been found (Fig. 6) in three available samples of facade jointing mortar. This means that some joints, for example like those of Fig. 2, have been repaired by filling the hollow outside space $(20-30 \text{ mm})$ with a Portland cement mortar, clearly a long time (at least one century) after the original building construction (18th Century).

Moreover, detectable traces of ettringite and thaumasite, as well as a significant amount of gypsum, have been found in all the available samples of this repairing jointing mortar (Fig. 7). Gypsum production, and its subsequent transformation into ettringite $(C_3A \cdot 3CaSO_4 \cdot$ $32H_2O$) and thaumasite $(CaSO_4 \cdot CaCO_3 \cdot CaSiO_3 \cdot$ $15H₂O$:

$$
3CaSO_4 \cdot 2H_2O + C_3AH_6 \xrightarrow{\text{water}}
$$

 $C_3A \cdot 3CaSO_4 \cdot 32H$, O (3)

 $CaSO_4 \cdot 2H_2O + CaCO_3 + CSH$ water

 $CaSO₄ \cdot CaCO₃ \cdot CaSiO₃ \cdot 15H₂O$ (4)

Fig. 6 Treated XRD pattern of a facade jointing mortar showing the presence of trace quantities of cement compounds.

Fig. 7 Treated XRD pattern of Portland cement based mortar sample to repair consumed facade jointing mortar.

could be ascribed to the formation process 2. Potential sulfate ion sources are (a) sulfate salts from bricks and (b) sea water capillary suction. In addition to these sources, gypsum could be formed by sulfur dioxide oxidation and subsequent sulfation of calcite [5-7], which is present both in the cement paste and in sand:

$$
CaCO3 + SO3 \xrightarrow{\text{water}} CaSO4 \cdot 2H2O + CO2 (5)
$$

The presence of $SO₂$ as a pollutant in the area of the Vanvitelli's Mole has been confirmed by an environment survey (see Section 2): the busy car traffic in the streets, the ferry boats in the harbour area, and a neighbouring industrial factory cause the environmental $SO₂$ content near Vanvitelli's Mole to be much higher than the legal limit in force locally. Therefore, gypsum formation [5-7] by sulfation process 5 cannot be excluded where significant amounts of gypsum have been found. Moreover, the fact that gypsum has been found clearly in the mortar facade jointing samples exposed to polluted air (Fig. 7) and only in traces in interior mortar samples (Fig. 4) would indicate that sulfation of calcite (see 5) is the process responsible for gypsum formation.

For ettringite or thaumasite formation, according to processes 3 or 4, the presence of humidity is also required [2]. In the specific case of Vanvitelli's Mole in Ancona, water can come through two different ways, both from the same source: (a) capillary rise through the foundation which is in contact with sea water and (b) evaporation from sea water. Capillary rise has been documented by excavation carried out in four different areas of Vanvitelli's Mole: the foundation consists of brick- or pozzolan-lime

concrete placed into a special formwork made by wooden piles driven into the shallow sea bed. Moreover, in the case of Vanvitelli's Mole no precaution has been taken to block the water capillary rise from the foundation as, for instance, is usually done [8, 9] in Venice where impermeable Istrian stones or lead plates have been inserted into the bottom of masonry walls of the buildings in contact with sea water. On the other hand, due to the local climatic conditions, the RH is much higher than in other maritime Italian towns [10, 11]: the average RH in Ancona is 77.2% versus 74% in Venice, and the maximum RH is 84.5% in Ancona, versus 81.1% in Venice, 65% in Trieste or 58% in Genoa.

Therefore, in the repair mortar of Vanvitelli's Mole, all the three requirements for ettringite and thaumasite production [2] have been documented in the present work: (a) calcium aluminate or silicate hydrates produced by hydration of Portland cement used to repair the surface of jointing mortars; (b) gypsum formation by reaction of environmental SO_2 with lime; and (c) presence of water produced by sea water capillary suction or capillary condensation of water vapour in humid air.

5.3 Rendering mortars

By XRD analysis, the five samples of rendering mortars have been separated into two types: (a) three samples based on lime-pozzolan mixes which do not contain any trace of gypsum, ettringite and thaumasite (Fig. 8a); and (b) two samples based on Portland cement mixes with traces of C_3S , C_2S , C_3A and C_4AF still present. In these

Fig. 8 Treated XRD patterns of three rendering mortars: A, without gypsum and ettringite or thaumasite; B, only gypsum (G); and C, gypsum (G), ettringite (E) and thaumasite (T).

two samples, two different situations have been found: in one sample a significant amount of gypsum is present without ettringite/thaumasite (Fig. 8b); in the other sample a significant amount of ettringite/thaumasite is present with a lower amount of gypsum (Fig. 8c). In the latter, it can be assumed that reactions 3 and 4 occurred, for some reasons, to a much higher extent than in the former: for instance, local humidity could have been higher in one area of the rendering mortar than in the other one, so that the degree of gypsum transformation into ettringite or thaumasite has been controlled by the local availability of water in the rendering mortar.

The presence of traces of C₃S, C₂S, C₃A and C₄AF in some areas of the rendering mortars (documented by a treated XRD pattern similar to that shown in Fig. 6) is clear evidence that an unsuccessful repair has already been tried using Portland cement: significant detachment of this repairing mortar is observed almost everywhere (Fig. 3). Besides the gypsum formation and the subsequent ettringite and/or thaumasite production, other physical events, such as salt crystallization, and thermal changes, cannot be excluded as responsible for the deterioration of the rendering mortars.

6. CONCLUSIONS

Lime-pozzolan mixes have been used for both the jointing mortar and the rendering mortar of the brick masonry wall in Vanvitelli's Mole erected in Ancona in the 18th Century. Physical events, such as rain water leaching out, thermal changes, freezing-thawing, salt

crystallization, etc., appear to be responsible for the deterioration of this mortar. A Portland cement based mortar has been used in the past to repair the deteriorated jointing mortar as well as the rendering mortar. This repairing mortar appears to have been damaged by ettringite/thaumasite formation, as local humidity and sulfate sources are available to react with calcium aluminate/silicate hydrates produced by Portland cement hydration. Environmental $SO₂$ appears to be the main source of sulfate salts in addition to those coming from brick impurities or sea water capillary rise. For future repair work, cementitious materials should be tested and proved to be resistant to sulfate attack before their utilization in this historic building.

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RESUME

Dégradation de mortiers de murs en maçonnerie dans les édifices historiques. Un exemple: Le Mole de Vanvitelli à **Ancona**

On a utilisé les résultats de techniques avancées, comme *'l'enhanced pattern treatment' de l'analyse de diffraction* des rayons x, combinés avec des données historiques et des *informations sur l'environnement, pour diagnostiquer le mécanisme complexe de dégradation d'un édifice historique.*

Cet article illustre le cas d'un fameux batiment italien \dot{a} Ancona, conçu et bâti par l'architecte napolitain Luigi *Vanvitelli entre 1733 et 1743, dans lequel les mortiers tant des joints que de l'enduit se sont très gravement détériorés.* On découvert que les mortiers originaux de chaux et pouzzolane se sont détériorés en raison de mécanismes *physiques (ravinement, amplitudes thermiques, gel et dégel,* etc.), alors que les mortiers de ciment Portland, employés pour réparer des murs détériorés ont été endommagés *par l'agression sulfatique.*