

# Degradation and restoration of masonry walls of historical buildings

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*Masonry walls have been tentatively classified according to all the possible combinations of the available original materials of historical buildings: lime, gypsum, hydraulic lime, stone, brick, etc. Fifty potential masonry walls of historical buildings have been assumed on this basis. The possible causes of chemical deterioration of masonries due to interactions among the original materials have been analysed: the potential reasons for chemical degradation are basically conducive to the alkali-amorphous silica reaction (in stones) and, above all, to sulphate salt reactions causing the formation of ettringite and/or thaumasite. In both cases, water plays a basic role in the course of the above-mentioned reactions: only in the presence of moisture - even occurring occasionally - have historical building masonries been subjected to significant deterioration. The recovery of historical buildings is a very delicate operation, since the materials employed in restoration work can interact negatively with some of the compounds that might be present in masonries. Owing to these reactions, the restoration operation can worsen the state of masonries. These reactions cause swelling, pop-out and falling of jointing and rendering mortars applied during the restoration work, as well as of cement grout injections for interior consolidation of structures. Again, ettringite and/or thaumasite may be found as deterioration products, provided that moisture is present in building masonries.*

## 1. INTRODUCTION: THE IMPORTANCE OF THE PROBLEM

The problem of the degradation and restoration of masonry walls, especially in historical buildings\*, has not yet drawn the due attention of engineers and researchers in the field of construction materials. This lack of concern is even more relevant when considering the analogous problem of the deterioration and restoration of reinforced and prestressed concrete structures, to which a large number of articles, seminars, congresses are devoted all over the world every year; yet the evidence of the cultural, architectural, social and economic importance of historical building recovery is clear when one thinks of the magnitude of this building heritage all over Europe.

The reasons for the discrepancy between the importance of the problem on one side, and the related lack of interest in investigating on the other, will not be analysed by this article. However, it has to be pointed out that, as a consequence of this lack of interest in investigating the problem, very often the consolidation and restoration of historical buildings end by increasing the degradation of masonry walls after the first period of apparent improvement. The reasons for these frequent accidents have a perfect parallel in medical science: very often a faulty diagnosis and the consequent therapy

make the health of the patient worsen, either because the causes of the disease are not removed by the therapy applied, or because the therapeutic treatment interferes negatively with the patient's pre-existing state.

Going back to the masonries of historical buildings, and to give only an example of incorrect restoration intervention, quite often the process of cementing (consisting in reinforcing the walls by cement injections or applying new cement-based mortars to restore old rendering mortars) ends by causing more damage than benefit because of the interaction of cement with the pre-existing materials (bricks, stones or original binders).

It must be pointed out that, even in the absence of old or more recent restoration work, negative interactions may have occurred among the various original materials, leading to severe deterioration of the structure. Another cause of degradation may be attributed to restoration work carried out in the past, prior to the 19th century (that is, before the advent of Portland cement).

Last, the third cause of degradation can be seen in recent restoration operations, mostly in the present century, because of negative interference of modern construction materials (Portland cement, epoxy resins, etc.) with the original materials or with those used in other repair work. This cause of degradation is certainly the most serious one, not only because of the practical and sometimes appalling effects obtained by an improper use of modern materials, but also from the cultural point of view, because ancient works have not been

studied and respected with humility, even though much more effective means, knowledge and technologies than in the past were available. Only by removing this cultural conceit will it be possible to face the cognitive investigation of ancient constructions and to suggest adequate technologies for their recovery by presently available materials.

This article will examine the types of masonry walls according to all possible combinations of the available original materials of historical buildings. This tentative classification aims to be a contribution to the knowledge of the past, and also a starting-point for subsequent research on the problem of the degradation of historical buildings.

## 2. CLASSIFICATION OF THE POSSIBLE TYPES OF MASONRY WALLS BASED ON THE MATERIALS ORIGINALLY USED

### 2.1 Construction materials in masonry walls of historical buildings

The construction materials originally used in the masonry walls of historical buildings consist of

- (i) binding materials (gypsum, lime, hydraulic lime);
- (ii) normal or pozzolanic sands for the manufacture of mortars;
- (iii) the elements to be bound (stones and bricks).

In the case of concrete walls, besides binder and sand, hewn stones and/or crushed bricks were used.

#### 2.1.1 Gypsum

Gypsum hemihydrate or plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) is a binder able to harden when mixed with water, forming gypsum dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). It hardens only in the air. It is used in the form of a paste (mixed with water only) for stucco or decorative work, or in the form of rendering mortar, mostly situated on the inside because of its capability of being washed away by rain water. It is also used in the form of mortar to bind bricks and stones (jointing mortar). Due to its low strength, gypsum has never been used in manufacturing concrete. For its ease of production (burning temperature about  $200^\circ\text{C}$ ), gypsum was the first binder to be used: as an example, the ancient Egyptians used gypsum as jointing mortar to connect the stones of Cheops' pyramid (2500 BC).

Although it is hardly known, gypsum was widely used in the mortars of the masonry walls of historical buildings, even after the introduction of lime, a technically better binder. The author of the present article has often found the presence of gypsum in masonry walls of historical buildings in Italy. Also Ludwig and Mehr [1] pointed out that, in Germany too, gypsum mortars were widely used in the masonries of historical buildings.

Moreover, it was often used in consolidation work in the form of a grout injected into masonry walls.

#### 2.1.2 Lime and pozzolan

Lime,  $\text{Ca}(\text{OH})_2$ , also hardens in the air only. When mixed with water, it reacts with the carbon dioxide of the air to form calcium carbonate ( $\text{CaCO}_3$ ). Especially in the past, lime was used as lime putty, that is a mixture of  $\text{Ca}(\text{OH})_2$  and water, obtained by mixing calcium oxide ( $\text{CaO}$ ) with an excess of water with respect to the chemical amount required to obtain calcium hydroxide,  $\text{Ca}(\text{OH})_2$ . The production of lime started long after that of gypsum because of the higher burning temperature (approximately  $900^\circ\text{C}$ ) of the limestone it comes from, and therefore, of the more difficult production process. Although evidence (Pliny the Elder) proves that the Egyptians knew how to produce lime, it was used on a large scale only later by the Greeks and above all by the Romans.

At the beginning, lime was used in the form of air-hardening mortar, by mixing lime, water and ordinary sand. Later, it was discovered that substituting ordinary sand by sand of volcanic origin (the type existing near Pozzuoli), mortar became hydraulic, that is it was able to harden also under water. The type of sand able to change an air-hardening mortar into a hydraulic mortar, though the binder used (lime) is air-hardening\* in itself, is defined as pozzolanic. The effect is principally due to the presence in pozzolan of silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) that react with lime because of their amorphous and vitreous state, in addition to their high specific surface area [2]. Very often the same effect was obtained by substituting ordinary sand with ground burnt clay or 'pounded earthenware' (finely ground bricks or tiles). Both sand of volcanic origin (natural pozzolan) and pounded earthenware (artificial pozzolan) react with lime, changing it into hexagonal hydrated aluminates ( $\text{C}_4\text{AH}_3$ )† and, above all, into a type of calcium hydrosilicate (C-S-H) which provides higher strength and, in particular, hardens under water [2].

Although the discovery of hydraulic mortars is commonly attributed to the Romans, it is believed that even the Phoenicians and the Israelites in the 10th century BC knew the technique of producing hydraulic mortars to protect all hydraulic works (aqueducts, ports, tanks,

\*Obviously this change from air-hardening into hydraulic mortar does not occur in gypsum mortars because pozzolan can react only with lime; therefore, in the mortars with gypsum, the use of ordinary or pozzolanic sand is unimportant as to the pozzolanic activity, that is, to the ability of providing higher strengths and, above all, of producing water-resistant compounds. However, the pozzolan in a gypsum-based mortar can react with the lime or hydraulic lime of adjacent mortars. For example, the gypsum-pozzolan rendering mortar of the masonry can interfere with the lime jointing mortar of bricks and stones; in this case, typical products of the pozzolanic reaction form at the interface of the two mortars between the pozzolan in the rendering mortar and the lime in the jointing mortar.

†According to the symbology of cement chemistry, C =  $\text{CaO}$ ; A =  $\text{Al}_2\text{O}_3$ ; H =  $\text{H}_2\text{O}$ ; S =  $\text{SiO}_2$ ; F =  $\text{Fe}_2\text{O}_3$ .

\*In this report the buildings constructed before the advent of Portland cement, at the end of the 19th century, are defined as 'historical'.

etc.) where washing used to deteriorate ordinary mortars rapidly. The drinking-water reservoirs King Solomon ordered to be built in Jerusalem were protected by hydraulic mortar obtained by mixing lime and pounded earthenware [3].

Even prior to the Romans, who surely realized the importance of pozzolan in hydraulic works or in constructions exposed to weathering and to the action of rain, the Greeks employed pozzolan, in the form of sand, especially through the use of volcanic ash from the island of Santorine. According to Lea [4], the use of pozzolanic materials – in the form of powdered calcined clay – dates back to 2000 BC in some structures in the island of Crete.

Above all, after the discovery of the hydraulic behaviour of lime and pozzolan mixtures, lime started being used in the manufacture of concrete by mixing lime, pozzolanic sand, water and hewn stones (*caementum*, the Latin word for cement)<sup>3</sup>. A large number of Appian Claudius Caecus' works in 300 BC, such as the Appian aqueduct and the Appian Way, give evidence of the use of real concrete because of hewn stones used as coarse aggregate [3]. The most famous example of a structure made of concrete containing lime and pozzolan is perhaps the great dome of the Pantheon in Rome (43 m in diameter). In most of the ancient Roman works, as a matter of fact, concrete was used as a filling between external brick or stone facings acting as permanent formworks.

### 2.1.3 Hydraulic lime

Several centuries passed before the discovery of a type of special lime that, independently of the presence of pozzolan, had by itself the ability to harden and resist the washing action of water. Such a special lime is called hydraulic lime.

In 1570 the Italian architect Andrea Palladio [5] made mention of an extraordinary lime obtained burning a calcareous stone with hydraulic properties near Padua. He stated: 'The lime obtained from this stone hardens

immediately and can be used both in works in contact with water and in works exposed to weathering'. Today we know that the hydraulic ability of the lime described by Palladio was due to the impurity in the starting limestone because of the presence of clay (marly limestone). In the presence of clay (rich in silica and alumina), dicalcium silicate ( $C_2S$ ) and monocalcium aluminate (CA) also form during burning, in addition to CaO. Then the product is treated with the right amount of water, chemically sufficient to transform CaO into  $Ca(OH)_2$  and leaving  $C_2S$  and CA to be anhydrous. When the hydraulic lime so obtained is mixed with water and sand,  $C_2S$  and CA react with water and are able to harden also under water [2]. Thus the first rudimentary modern cement, which owes its high-strength and hydraulicity properties to the presence of calcium silicates and aluminates, was started to be manufactured, even though unwittingly.

In the mid-18th century, Juvara and other Savoyard architects knew well the different performance of 'weak lime mortar' – lime – and 'strong lime mortar' – hydraulic lime, the former being used in inside rendering mortars, the latter in more exacting work demanding higher strength and watertightness [6].

Some time elapsed, however, before getting to the rational and scientific production of hydraulic limes first, and of Portland cement later. Only after the Industrial Revolution and, above all, the beginning of modern chemistry with Lavoisier, around the mid-18th century, was the chemical analysis of the stones from which binders were produced by burning started, together with the rational, industrial choice of producing one type of binder rather than another one.

However, from a practical point of view the hydraulic mortars widely used since the mid-18th century, containing hydraulic lime, water and normal sand, do not show – once hardened – significant differences from the old hydraulic mortars developed by the Romans and consisting of lime, water and pozzolan. Even chemically, they look very much alike, since the material imparting hydraulic ability, besides higher strength, is the above-mentioned calcium hydrosilicate (C-S-H). It forms either by the reaction of lime with pozzolan, or by the hydration of the silicate ( $C_2S$ ) that is present in the hydraulic lime.

To conclude the evolution history of hydraulic lime, the way of producing it in recent years must be explained [7,8]. Up to the prewar period, hydraulic lime was manufactured by burning marly limestone (natural hydraulic lime) or mixtures of pure limestone and clay (artificial hydraulic lime). After that, artificial hydraulic limes were produced, 'diluting' Portland cement by a mixture of finely ground aggregate (filler) or, alternatively, by mixing a hydraulic binder (Portland cement) with an air-hardening binder (lime) to produce the so-called 'spurious' mortars, greatly appreciated for their plasticity. At present, artificial hydraulic lime is produced by mixing Portland cement, filler and air-entraining admixtures that, developing about 15% of air

Table 1 Types of masonry

Brick masonry (B)		Stone masonry (S)		Concrete masonry (C)	
Exposed to view	With rendering mortar	Exposed to view	With rendering mortar	Exposed to view	With rendering mortar
<i>Be</i>	<i>Bm</i>	<i>Se</i>	<i>Sm</i>	<i>Ce</i>	<i>Cm</i>

in volume, impart to the mortar the 'fatness' and plasticity (usually due to the presence of lime) that used to be found in good hydraulic limes. At present, hydraulic lime (actually Portland cement 'diluted' with filler and air) has almost completely substituted the use of lime in rendering coat works as well.

### 2.1.4 Stones

The stones<sup>3</sup> used in masonries do not show special problems as to the interaction with the binders originally used in the construction of historical buildings (gypsum, lime, hydraulic lime) apart from the potential alkali-aggregate reaction in the technology of concrete [2]. The reaction may occur between the alkalis (sodium and potassium) of the binder and some minerals potentially present in stones (amorphous silica in the form of opal or chalcedony or dolomite).

### 2.1.5 Bricks

Bricks are obtained by burning clay previously shaped and dried. Owing to the presence of determinate minerals (pyrite, above all) in the raw materials [7], bricks may contain some salts (nitrate, chloride, phosphate and, in particular, sulphate) of alkaline (sodium and potassium) and alkaline earth (calcium and magnesium) metals, that are easily soluble in water [9].

On account of wetting (by rainwater, for instance) and subsequent drying, water can first penetrate the brick and dissolve salts. Then the aqueous solution comes back and on evaporating deposits the salts on the brick surface. If the brick surface is exposed to view, typical salty efflorescences will be noticed. If the brick is coated by rendering mortar, the salts deposited on the brick surface as a matter of fact lie at the brick-mortar interface. In this case, the physical-mechanical effect may cause the disjunction of the mortar, or even more serious deterioration may occur due to the reaction between salt and mortar. Three types of degradation may occur [2]: (a) the reaction between the alkalis of salts and the reactive aggregate of mortar (alkali-

aggregate reaction); (b) the reaction among the sulphates and hydrated calcium silicates (C-S-H) present in hydraulic limes (production of thaumasite); (c) the reaction between sulphates and hydrated aluminates, present in hydraulic limes (production of ettringite). All three reactions may take place with higher intensity and more severe damage when the mortar is cement-based, as often happened in recent restoration and consolidation work.

### 2.3 The types of historical building masonry walls according to construction materials

According to the combination of construction materials, the following masonry types may occur: brick masonry (B), stone masonry (S), and concrete masonry (C); in addition, each of them may be exposed to view (e) or coated with rendering mortar (m). Table 1 sums up the different masonries according to this classification. For example, *Se* indicates exposed-to-view stone masonry, while *Sm* stands for stone masonry coated with rendering mortar.

In theory, each type shown in Table 1 (*Be*, *Bm*, *Se*, etc.) can have an 'inside' binder (i.e. in the jointing mortar or in the concrete), based on lime (l) or gypsum (g). As a matter of fact, the binder used in concrete has always been lime only. Moreover, lime can be used with normal sand to produce air-hardening mortar (l) or with pozzolanic sand to produce hydraulic mortar (l'). On the basis of the above considerations, 20 different types of masonry can be classified, as shown in the upper parts of Table 2 (brick masonry), Table 3 (stone masonry) and Table 4 (concrete masonry). For example, *Beg* in Table 2 indicates a brick masonry (B), exposed to view (e), containing sand and gypsum (g) as binders in jointing mortar; in Table 3 *Sml* and *Sml'* indicate respectively stone masonry (S) coated with rendering mortar (m) and with lime and sand (l), or lime and pozzolan (l') in jointing mortar.

Rendering mortar may consist of gypsum and sand (g), gypsum and pozzolan (g'), lime and sand (l), or lime and pozzolan (l'). With this further classification, we get to 50 different masonries shown in the bottom parts of Tables 2, 3 and 4. For example, *Bmg'l* in Table 2 indicates a brick masonry (B) coated with rendering mortar (m), with sand and gypsum as 'inside' binder in jointing mortar (m), and sand and lime as 'outside' binder in rendering mortar (l). Again, in Table 4, *Cml'* indicates a concrete masonry (C), coated with rendering

<sup>3</sup>Concrete masonries were widely constructed in ancient times and are cited in Pliny the Elder ('Natural History') and Pollio Vitruvius' works ('De Architectura'). Concrete (*opus caementitium*) would consist of crushed stones or bricks, mixed with lime, sand and water. In hydraulic works, sand would be substituted by natural pozzolan or pounded earthenware (artificial pozzolan). Crushed stones used in manufacturing concrete would be called in Latin, even by the Roman writers Livius and Cicero, *caementum*, from the verb *caedere*, meaning to hew. It is interesting to observe, according to Gorla [3], the peculiar etymological change of the word *caementum*: after becoming *caementum* in the passage from classical to vulgar Latin, originally the word still had the meaning of hewn stone, while later, through a typical synecdochical process, it assumed the meaning of the whole conglomerate, that is, made of water, binder, sand and hewn stones, which today is defined as concrete. In substance, up to the Middle Ages, the word cement (in Italian *cemento*) would indicate what is correctly called concrete today. Only at the end of the 18th century in the Italian language did the word *cemento* assume the present meaning of binder. Lastly, the English word 'concrete' also comes from the Latin *concretum*. Cicero wrote '*concretum corpus ex elementis*', meaning a body composed of different elements, thus including the meaning of conglomerate.

<sup>3</sup>Stones used in the various stone masonries are mostly square and relatively big (*saxum quadratum*, according to Vitruvius), while hewn stones in concrete masonries have irregular shape, relatively small size (not bigger than a hand, according to Vitruvius) and suit the manufacture of *saxum caementitium*, that is a unit made of hewn stones with lime and water as binders.

Table 2 Types of brick masonry

Brick masonry exposed to view (Be)				Brick masonry with rendering mortar (Bm)			
Joining mortar		'Inside' binder: gypsum		'Inside' binder: lime†		'Inside' binder: gypsum	
Ordin. sand	Pozzol. sand*	Ordin. sand	Pozzol. sand	Ordinary sand	Pozzol. sand	Ordinary sand	Pozzol. sand
Beg	Beg'	Bel	Bel'	Bmg	Bmg'	Bmg	Bmg'
Rendering mortar				'Outside' binder: gypsum	'Outside' binder: lime	'Outside' binder: gypsum	'Outside' binder: lime
Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
Bmgg	Bmgg'	Bmgl	Bmgl'	Bmg'g	Bmg'g'	Bmg'l'	Bmg'l'
				'Inside' binder: lime			
				Ordinary sand	Pozzol. sand		
				Bml	Bml'		
'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
Bmlg	Bmlg'	Bml	Bml'	Bml'g'	Bml'g'	Bml'l'	Bml'l'

\*Pozzolanic sand is intended as either natural sand, generally of volcanic origin, or artificial sand, obtained by fracturing bricks, tiles, etc. ('pounded earthenware').  
 †In practice, using hydraulic lime instead of ordinary lime, mortar becomes hydraulic even in the absence of pozzolan; in other words, Bel becomes Bel' when hydraulic lime is used.  
 ‡Indicates brick masonries deteriorated by sulphate attack (see Section 3 and Figs 2 and 3).  
 §Indicates brick masonries deteriorated by sulphate attack (see Section 3 and Figs 2 and 3) only in the case of bricks containing sulphate salts.

Table 3 Types of stone masonry

Stone masonry exposed to view (Se)				Stone masonry with rendering mortar (Sm)			
Joining mortar		'Inside' binder: gypsum		'Inside' binder: lime†		'Inside' binder: gypsum	
Ordin. sand	Pozzol. sand*	Ordin. sand	Pozzol. sand	Ordinary sand	Pozzol. sand	Ordinary sand	Pozzol. sand
Seg	Seg'	Sel	Sel'	Smg	Smg'	Smg	Smg'
Rendering mortar				'Outside' binder: gypsum	'Outside' binder: lime	'Outside' binder: gypsum	'Outside' binder: lime
Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
Smgg	Smgg'	Smg	Smg'	Smg'g	Smg'g'	Smg'l'	Smg'l'
				'Inside' binder: lime			
				Ordinary sand	Pozzol. sand		
				Sml	Sml'		
'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
Smlg	Smlg'	Sml	Sml'	Sml'g'	Sml'g'	Sml'l'	Sml'l'

\*Pozzolanic sand is intended as either natural sand, generally of volcanic origin, or artificial sand, obtained by fracturing bricks, tiles, etc. ('pounded earthenware').  
 †In practice, using hydraulic lime instead of ordinary lime, mortar becomes hydraulic even in the absence of pozzolan; in other words, Sel becomes Sel' when hydraulic lime is used.  
 ‡Indicates stone masonries deteriorated by sulphate attack (see Section 3 and Figs 2 and 3).

Table 4 Types of concrete masonry

Concrete masonry exposed to view (Ce)		Concrete masonry with rendering mortar (Cm)			
'Inside' mortar		'Inside' binder: lime		'Inside' binder: lime	
Ordin. sand, hewn stone	Pozzol. sand, hewn stone	Ordinary sand, hewn stone	Pozzol. sand, hewn stone	Ordinary sand, hewn stone	Pozzol. sand, hewn stone
Cel	Cel' <sup>‡</sup>	Cml	Cml'	Cml	Cml'
Rendering mortar		'Outside' binder: gypsum	'Outside' binder: lime	'Outside' binder: gypsum	'Outside' binder: lime
Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
Cmlg	Cmlg' <sup>‡</sup>	Cml	Cml'	Cml'g' <sup>‡</sup>	Cml'g' <sup>‡</sup>

†In practice, using hydraulic lime instead of ordinary lime, mortar and concrete become hydraulic even in the absence of pozzolan; in other words, Cel becomes Cel' when hydraulic lime is used, even in absence of pozzolan sand.  
 ‡Pozzolanic sand is intended as either natural sand, generally of volcanic origin, or artificial sand, obtained by fracturing bricks, tiles, etc. ('pounded earthenware').  
 §Indicates concrete masonries deteriorated by sulphate attack coming from rendering mortar.  
 ¶Indicates concrete masonries deteriorated by sulphate attack coming from hewn bricks or stones.

mortar (m), with lime and sand in the 'inside' concrete mortar (l), and lime plus pozzolan in the 'outside' rendering mortar (l').

The classification presented in the present article, founded on materials used, has nothing to do with a classification of the types of masonry based on architectural-structural criteria, such as for instance those presented by J. P. Adam in his most interesting book on ancient Roman constructions [10].

In addition, when the masonry is complex from the constructional point of view, the above classification will refer to the part of the wall where deterioration has appeared. For example, a complex masonry composed of concrete filling with lime and pozzolan-based binder (l'), coated by stone facings with gypsum-based binder (g), plastered itself by normal sand and lime mortar (l), will be classified as Cml'g, or as Smgl according to whether attention is turned to the inside masonry (Cml'g) deterioration or to the surface masonry (Smgl) deterioration. In fact, concrete will be classified as if it were rendered by the gypsum mortar (g), that, in reality, acts as jointing mortar for stones.

### 3. CHEMICAL CAUSES OF DEGRADATION OF ORIGINAL MATERIALS

#### 3.1 Chemical and physical causes of degradation

Apart from structural causes, where masonries are subject to excess stress with respect to their strength, the mechanisms that caused the deterioration of historical building masonries, before any intervention by restora-

tion work, can be attributed to chemical and/or physical causes. Chemical causes are mostly connected with the reactions between sulphate and the other compounds in the masonry. Physical causes are mainly, not exclusively, due to physical variations of water inside masonry: evaporation, capillary flow, ice formation, etc. [11].

Only chemical causes will be examined in the present work, while physical causes will be analysed in a later paper. However, it is important to point out immediately that water plays a role of the utmost importance even in chemical causes for two reasons:

- (a) first of all, water - in the liquid form or as vapour - is actively involved in all the chemical reactions that may have caused degradation, as will be seen later on;
- (b) secondly, water in the form of liquid has the important function of carrying one component towards the other, thus providing a physical contact between the two components, without which the chemical reaction between them could not have occurred; think, for instance, of water that, in its capillary flow inside masonries, carries a hydrosoluble salt - present in bricks, for instance - and puts it in contact with rendering mortar; this would allow a 'dangerous' chemical reaction to take place between the salt and the component in the rendering mortar.

Consequently, even the discontinuous presence of moisture in masonries is a necessary, even if not sufficient, condition to start degradation, not only due to physical causes, but also based on chemical interactions. Moreover, the masonries that have always been kept dry have not been subjected to any chemical degradation,

even if potentially 'dangerous' elements inside them might have interacted chemically to produce deteriorating compounds in the presence of moisture.

### 3.2 Masonry classification according to materials

In order to investigate all the chemical reactions that may have caused the degradation of historical building masonries, a classification of the potential masonry types has been proposed in Section 2. In Tables 2, 3 and 4 above (corresponding to brick, stone and concrete masonries, respectively) the types of masonry subject to potential deterioration (depending on mechanisms explained later) are also indicated.

Note that, for the purpose of the present classification, a lime mortar is considered to be hydraulic either when lime is used in the presence of a pozzolanic sand or when hydraulic lime is used in combination with any type of sand. In the case of gypsum coupled to a pozzolanic sand instead of ordinary sand, the performance of the binder does not change from an air-hardening into a hydraulic one; however the two mortars (*g* and *g'*) must be distinguished, in order to understand the deterioration mechanism described hereafter.

### 3.3 'Dangerous' chemical reactions among original materials: the sulphate attack

The main chemical reactions that have caused masonry degradation, as a consequence of the interaction among original materials, are basically two, and both require the presence of sulphate, in addition to moisture [1]. The

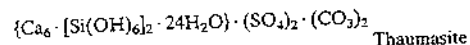
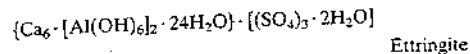
products that may be originated by these reactions are ettringite and thaumasite, two well-known compounds in Portland cement chemistry [12]. However, they can also form in the materials of historical buildings constructed before Portland cement was discovered.

Both the formation of ettringite and that of thaumasite appear macroscopically (Fig. 1) through swelling of the original material that can scale or be reduced even to pulp when thaumasite is produced. Quite often the two compounds are both present, although usually the formation of ettringite precedes that of thaumasite. Moreover, both compounds have the characteristics of being produced at cold ambient temperatures (0 to 10°C) more rapidly than in hot conditions.

It is important to emphasize that the formation of ettringite is not dangerous in itself, that is, it does not originate swelling if it is not accompanied by the presence of lime. Mehta [13] proved that when it forms in basic surroundings, due to the presence of lime, ettringite crystallizes in the form of very short (a few micrometres), badly grown fibres, able to absorb water and cause swelling. Conversely, when lime is absent, ettringite shows well-grown fibres (about 100 µm long) that do not absorb water and cause swelling. Mehta defines as 'colloidal' or 'crystallized' ettringite able or unable, respectively, to cause swelling.

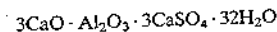
Chemical compounds can have two types of formula: structural formulae and 'raw' formulae. The former type relates to the structural and crystallographic aspects (i.e. it shows how atoms are co-ordinated inside the crystal patterns). Structural formulae of ettringite and thaumasite show the close resemblance between these two products. This could explain the analogy between

ettringite and thaumasite formation processes and degradation mechanisms:

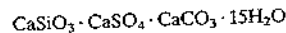


In short, in the crystal pattern of thaumasite the silicon ion occupies the place occupied by the aluminium ion in the crystal pattern of ettringite. However, due to the different electric charge of silicon ( $Si^{4+}$ ) with respect to aluminium ( $Al^{3+}$ ), in addition to the sulphate ion ( $SO_4^{2-}$ ), thaumasite needs the carbonate ion ( $CO_3^{2-}$ ) to neutralize the positive electric charges in the crystal pattern.

The 'raw' formulae inform us of the compounds (calcium sulphate, calcium silicate, etc.) the two products are made of, but they have nothing to do with the crystallographic aspect. However, they are very useful because they are indicative of the compounds that may originate the final products. For example, the 'raw' formula of ettringite is



while the 'raw' formula of thaumasite is



From the 'raw' ettringite formula, for instance, we know that it may form by the reaction of calcium sulphate, water and hydrated calcium aluminates, present in Portland cement mortars, or in hydraulic lime mortars, or in lime-pozzolan mortars ( $4CaO \cdot Al_2O_3 \cdot 13H_2O$ ,  $3CaO \cdot Al_2O_3 \cdot 6H_2O$ , etc.). From the 'raw' thaumasite formula we know that it may form from the reaction of calcium carbonate, calcium sulphate, water and hydrated calcium silicates, such as those present in cement mortars, in hydraulic lime mortars and in lime-pozzolan mortars. The composition of hydrated calcium silicates may vary and they can be associated with the general formula  $xCaO \cdot ySiO_2 \cdot zH_2O$ , sometimes also indicated, in short, C-S-H.

As far as non-restored historical building masonries are concerned, where the absence of Portland cement mortars is sure, it is clear that the formation of ettringite and/or thaumasite requires the concurrent presence of:

- (i) Calcium sulphate
- (ii) Water
- (iii) Lime-pozzolan mortars or hydraulic lime mortars, as they are sources of calcium aluminates and hydrated calcium silicates; even a plain lime mortar (for instance, in the rendering mortar) could act as a source of ettringite and/or thaumasite if pozzolan was used (for

instance in the jointing mortar) in the gypsum mortar: in such a case, at the interface of the two mortars, calcium aluminate and hydrated calcium silicates are formed by the reaction of lime with pozzolan.

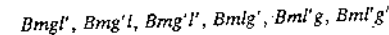
Figs 2 and 3 show schematically the possible chemical interactions among the different elements of masonries that may have contributed to the formation of ettringite and/or thaumasite. In Tables 2, 3 and 4 above the masonries that may deteriorate due to ettringite and/or thaumasite formation are indicated (see footnotes to tables).

### 3.4 Brick masonry degradation

In the following paragraphs, the causes of chemical degradation of brick masonries are investigated separately.

#### 3.4.1 Deterioration of masonry by sulphate attack independently of brick sulphate content

The brick masonries that deteriorate due to the chemical reactions shown in Fig. 2, independently of the content of sulphate salts in bricks, are the six following types:



In Table 2 the above types are marked (\*), gypsum being always present either in jointing mortar (*Bmg'l'*, *Bmg'l*, *Bmg'l'*) or in rendering mortar (*Bmg'l*, *Bml'g*, *Bml'g'*), associated with hydraulic lime in rendering mortar or in jointing mortar, respectively. In other words, the two mortars (jointing mortar and rendering mortar) are always complementary for the formation of ettringite and/or thaumasite in moist masonries.

Actually, two of the above-mentioned types (*Bmg'l'* and *Bmg'l*) do not contain hydraulic lime, but lime (*l*) among bricks (*Bmg'l*) or in rendering mortar (*Bmg'l'*). Therefore, in theory, we cannot assume in lime mortars the presence of hydrated calcium aluminates or hydrated calcium silicates that are essential for the production of ettringite (Fig. 2) and/or thaumasite (Fig. 3), from the reaction with gypsum. However, gypsum was used together with a pozzolanic sand (as a matter of fact the code used is *g'*, not *g*), even if, in the specific case, the sand did not develop its pozzolanic activity on gypsum. However at the interface of jointing and rendering mortars, there is lime on one side and pozzolan and gypsum on the other; this allows the formation of ettringite and/or thaumasite to take place.

#### 3.4.2 Deterioration of masonries by sulphate salts in bricks

Table 2 shows four brick masonries whose codes (*Bel'*, *Bml'*, *Bml'l*, *Bml'l'*) are marked (\*). Due to the absence of gypsum (as 'inside' or 'outside' binder), these masonries should not deteriorate, unless gypsum forms

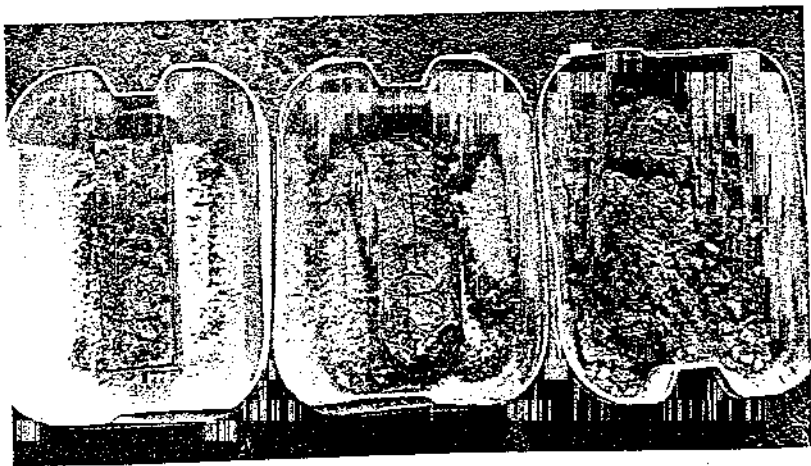


Fig. 1 From left to right: sound, deteriorated and destroyed mortar specimens arising from the formation of ettringite and thaumasite.

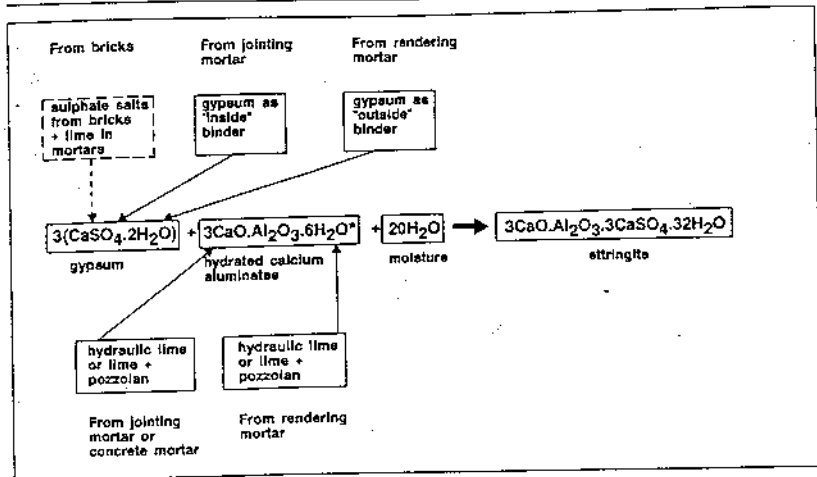


Fig. 2 Diagram of the possible interactions among masonry elements for the formation of ettringite. The interrupted line frame only concerns brick masonries containing sulphate salts. \*This hydrated calcium aluminates can be substituted by other hydrated calcium aluminates, e.g.  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ .

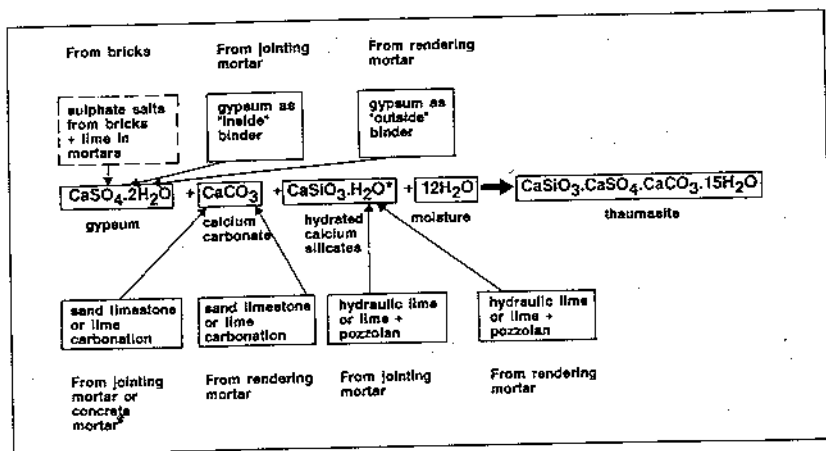
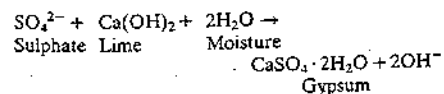


Fig. 3 Diagram of the possible interactions among masonry elements for the formation of thaumasite. The interrupted line frame only concerns brick masonries containing sulphate salts. \*This hydrated silicate represents the hydrated calcium silicates of the formula  $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$  (C-S-H).

*in situ* for the reaction between the sulphate into bricks ( $\text{SO}_4^{2-}$ ) and the lime into mortars:



This deterioration mechanism is shown in Figs 2 and 3 by interrupted lines. This type of degradation is frequent in the masonries built with bricks manufactured with clay contaminated by pyrite ( $\text{FeS}_2$ ) that, in the burning kiln, changed into the sulphate [9] of an alkali metal (potassium, sodium) or alkaline-earth metal (calcium, magnesium).

Sometimes, the presence of sulphate is evidenced by the formation of salty efflorescences. When this occurs, very often the appearance of efflorescences is followed by the deterioration of rendering mortars or jointing mortars, whenever hydraulic mortar (I') was used outside and/or inside the masonry, respectively. Also in these cases, in fact, ettringite and/or thaumasite can form according to the reactions shown in Figs 2 and 3 (interrupted line).

Also in this type of deterioration, moisture in the masonry plays a determinant role: the rain that wets masonries, or the capillary flow of water from foundations, dissolves the soluble salts into bricks and carries them towards rendering mortar when, subsequently, water evaporates towards the outside dry ambient atmosphere. So, even small amounts of sulphate salts in bricks mostly collect near the outside rendering mortar, thus creating crucial concentrations for the formation of ettringite and/or thaumasite if hydraulic lime or lime with pozzolan was used in the rendering mortar.

stone masonries (Smgl', Smg'l, Smg'l', Smgl', Sm'l'g, Sm'l'g') are less than those in brick masonries. In Table 3 the codes of the stone masonries attackable by sulphates are indicated. The reasons for deterioration are exactly the same as for the brick masonries discussed in Section 3.4.1.

### 3.5.2 Stone masonry deterioration due to the alkali-silica reaction

Stone masonries might suffer another type of chemical degradation that does not involve the presence of sulphates. This is based on the reaction between alkalis, present in mortar, and a few forms of reactive silica (opal, chalcedony, etc.), present in stones. The reaction - leading to the formation of very bulky hydrated alkaline silicates ( $x\text{Na}_2\text{O} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$ ) - is well known in cement chemistry under the name of 'alkali-aggregate reaction', since it occurs between cement alkalis and aggregates containing reactive forms of mostly amorphous silica [14].

The alkali-silica reaction, like that with sulphate, requires the presence of water and, therefore, might occur only in moist masonries, as illustrated in Fig. 4. This type of deterioration, although chemically different with respect to sulphate attack, apparently occurs analogously, with cracks, disjunctions, etc. The phenomenon is slower than with sulphate attack, but this is of negligible importance considering how long historical buildings should last.

### 3.5 Deterioration of stone masonries due to chemical causes

In stone masonries two types of potential deterioration due to chemical causes must be considered: the sulphate attack and the alkali-silica reaction.

#### 3.5.1 Stone masonry deterioration due to sulphate attack

The sulphate attack in stone masonries is simpler because it does not include the sulphate coming from stones, as frequently occurs in brick masonries (Section 3.4.2). Therefore, the mechanisms of stone masonry deterioration caused by sulphate relate only to the presence of gypsum used as binder in the original building.

Consequently, the possible cases of sulphate attack to

In the present article the reactions that cause stone deterioration due to the presence of sulphur dioxide in the environment, and the consequent formation of calcium sulphate, have not been treated. In this case, sulphatization and consequent deterioration involve not only masonries made of stones exposed to view, but also monuments, statues, or other masonry works without mortar. In other words, stone sulphatization is con-

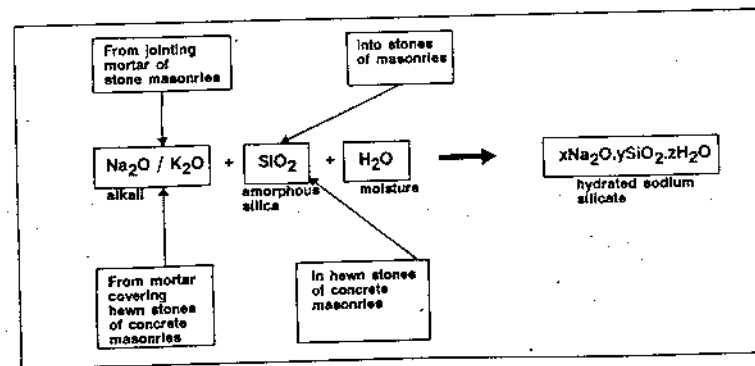


Fig. 4 Diagram of possible interactions among elements of stone or concrete masonries due to the alkali-amorphous silica reaction.

nected with the stone-environment interaction, and not the stone-mortar interaction, as occurs in the masonries considered by this article.

### 3.6 Concrete masonry deterioration due to chemical causes

Also in the concrete masonries of historical buildings, as with stone masonries, two types of attack are possible: sulphate attack and the 'alkali-silica' reaction.

#### 3.6.1 Concrete masonry deterioration due to sulphate attack

Since the use of gypsum as 'inside' binder of concrete masonries in historical buildings has been excluded (Section 2.1.1), the number of possible types is lower than with other masonries (Table 4). Basically, there are two causes of sulphate attack on concrete masonries of historical buildings.

The first cause is the presence of gypsum as 'outside' binder in rendering mortar: the masonries involved in this type of deterioration are Cmlg', Cml'g and Cml'g', that are marked \* in Table 4. Deterioration causes are exactly the same as those discussed in detail in brick masonries (Section 3.4.1) through the mechanism shown in Figs 2 and 3.

The second cause of deterioration due to sulphate attack is related to the possible presence of sulphate - mostly in the form of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) - in crushed bricks or stones\*. The masonries involved by this type of sulphate attacks are marked (b) in Table 4. They are Cel', Cml'I, Cml'I', in addition to Cml'g and Cml'g' that might be attacked also by the sulphates coming from rendering mortar. Even in this case the final products of the deterioration reaction are ettringite and thaumasite, that form because of the interaction of gypsum in crushed bricks or stones respectively with hydrated calcium aluminates and hydrated calcium silicates, present in hydraulic mortars inside concrete.

#### 3.6.2 Concrete masonry deterioration due to the alkali-silica reaction

This type of degradation is very similar to that described in Section 3.5.2 in stone masonries. Also in the concrete of historical buildings the reaction between the alkalis present in mortar and crushed stones may occur, wherever these contain reactive amorphous silica. The mechanism of the reaction is shown in Fig. 4.

### 3.7 Conclusion

Fifty possible masonry walls of historical buildings have been assumed on the basis of potential combinations of original construction materials: lime, hydraulic lime,

\*Gypsum or anhydrite may potentially contaminate natural stones used as aggregates in modern Portland cement concretes; there are standards in fact that absolutely exclude its presence.

gypsum, bricks, stones, etc. The possible causes of chemical deterioration of masonries due to interactions among original materials have been analysed: all possible reasons for chemical degradation are basically conducive to the alkali-amorphous silica (in stones) reaction and, above all, to sulphate salt reactions causing the formation of ettringite and/or thaumasite.

In all cases, water plays a basic role for the course of the above-mentioned reactions: only in the presence of moisture - even occurring occasionally - have historical building masonries been subjected to significant deterioration.

## 4. CHEMICAL DEGRADATION CAUSED BY RESTORATION WORK ON HISTORICAL BUILDING MASONRIES

### 4.1 The materials for restoration work

The materials used in the restoration of historical building masonries mainly belong to two categories: (a) materials similar to the original ones; (b) the 'new' materials available, since the end of the last century, that is, when the use of first Portland cement and later polymeric resins was started.

According to a widespread bias, only the use of materials similar, even identical, to those employed in the original construction would result in technically successful restoration work.<sup>†</sup> This is not always true. Historical buildings deteriorated significantly also before they were restored, sometimes because of the use of the original materials.

#### 4.1.1 Original materials in historical building masonries

We have seen that the materials originally used in historical buildings are mainly lime, gypsum, sand, pozzolan, bricks and stones. As to binders, both lime and gypsum harden only in the air, are not able to produce mechanically resistant mortars and, especially in outside rendering mortars, cannot resist the leaching action of rain.

##### 4.1.1.1 Lime

Although mechanically more resistant than gypsum, lime too is a weak binder. Lime mortar is leached by rainwater, is porous, and therefore water-permeable. If, on the one hand, this property favours the coming out of moisture that can be inside the masonry, on the other hand it does not protect masonries against water penetration from outside.

Only when combined with pozzolan, instead of ordinary sand, can lime harden significantly and produce mortars resisting the action of rainwater (hydraulic

<sup>†</sup>Obviously, this merely technical evaluation does not take into consideration historical-cultural reasons, according to which similar or identical materials, with respect to original ones, should be used in restoration work wherever possible.

mortar). The products deriving from the reactions among lime, pozzolan and water are similar to the products deriving from the reaction of water with the most modern hydraulic binders (cement and hydraulic lime). Subsequently, the discovery of hydraulic lime allowed the production of strong mortars, resisting the action of water even in the presence of ordinary sand instead of pozzolan.

##### 4.1.1.2 Gypsum

Conversely, gypsum, even in the presence of pozzolan, remains a weak binder and is unable to resist the leaching action of water. Nevertheless, for a long time, gypsum was used in many historical constructions. As mentioned earlier, the presence of gypsum as binder in historical building masonries was found by the author inside a large number of historical masonries in Italy.<sup>‡</sup> Its use in many other European countries cannot be excluded either. Ludwig and Mehr [1], for example, found important traces of gypsum inside the masonries of numerous historical buildings in Northern Germany.

The wide use of gypsum as a binder in jointing mortars, notwithstanding its lower performance with respect to lime, is not surprising. First of all, the production of gypsum as binder was easier and cheaper. Secondly, in ancient times the lack of the presently available means of communication would prevent the exchange of information on the technological performances of materials. Last, only the coming of modern chemistry allowed the scientific and sure distinction between limestone and gypsum, which, once burnt, produce lime and binding gypsum, respectively. Only in 1780 did the Berlin chemist A. S. Margraff discover the chemical composition of gypsum [3]; before then it had often been confused with limestone, although the different burning temperature was known empirically. Moreover, thanks to its relatively quick-setting characteristics, gypsum was consciously used in the past (but not only in the past!) to rapidly fix metal bars into masonries to restore them.

In addition to the reasons concerning the use of gypsum as a binder, there are other important elements justifying the presence of gypsum in historical building masonries. For example, bricks in historical buildings, as well as in modern constructions, contain considerable amounts of sulphate salts [9] sometimes showing themselves in the form of crystalline efflorescences. In contact with lime or limestone in mortar, these salts produce bihydrated calcium sulphate, that is, gypsum. Crammond [15], for example, found that considerable amounts of sulphate can be observed even in modern brick masonries.

Last, in constructions immersed in seawater or brackish water, as in Venice, for instance, sulphates from seawater flow into the capillary voids of the masonry<sup>§</sup>

<sup>‡</sup>The use in the past of gypsum as binder for outside rendering mortars, if any, cannot be checked today just because of the ease with which it is leached by rain.

walls and produce gypsum when in contact with lime or limestone of mortar.

### 4.1.2 Materials available for restoration work

Among the 'new' materials available today, those significantly different from original materials are: hydraulic lime, cement and polymeric resins.

Obviously, the binders employed in original masonries can also be used in restoration work: lime, gypsum and the lime-pozzolan mixture. According to the purpose of this article, the performance of the lime-pozzolan mixture is the same as that of hydraulic lime or Portland cement, since its hydration products contain hydrated calcium silicates and aluminates (Section 2) that can interact negatively with sulphates in masonries, as shown in Section 4.2 below. Lime and gypsum present the limit of being leached by rain easily, especially when they are used in outside rendering mortars. Moreover, as is shown in Section 4.2, they can also interact negatively with the other pre-existing components of the masonry.

#### 4.1.2.1 Hydraulic lime and cement

The hydraulic lime produced in the past and used also by the Italian architect Andrea Palladio used to be obtained by burning marl limestone, that is, by natural mixtures of limestone and clay. It was mainly composed of calcium hydroxide,  $\text{C}_2\text{S}$  and CA. The hydraulic performance of the binder, that is, the ability of hardening also under water and resisting the leaching action of rain [16], is due to the presence of the two above-mentioned compounds -  $\text{C}_2\text{S}$  and CA - present in Portland cement and aluminous cement, respectively. At present, very often hydraulic lime is really Portland cement diluted with filler. Moreover, it contains also an air-entraining agent for producing mortars whose plasticity is similar to that obtainable by the hydraulic lime produced in the old days, thanks to the presence of a significant volume of air [8].

In any case, from the standpoint of the possible interactions with original materials, there is no substantial difference between the presently available hydraulic lime and that produced in the past: both binders contain mineralogical compounds with hydraulic performance:  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  in the first case, and  $\text{C}_2\text{S}$  and CA in the second one [16]. As will be shown further on, the hydration products of these mineralogical compounds are responsible for the interference with other compounds in original masonries and, in particular, with sulphate salts. Also pozzolan or slag cements, that contain the same mineralogical constituents as Portland cement, together with pozzolan or blast furnace slag, respectively, behave like Portland cement.

#### 4.1.2.2 Polymeric materials

Polymeric materials are present in the form of aqueous latexes (based on vinyl acetate, acrylate, etc.), mixed



with mineral charges (kaolin, marble in powder form, dyes, cement, etc.) to form a dispersion to apply as paint or as a final finishing coating on masonry mortar.

The thin coating hardens due to water evaporation and the polymer, strongly adhering to the substrate, provides the masonry with a thin watertight charge; also cement hydration itself contributes to the coating action: in this case, according to polymer/cement and water/cement ratios the coating may be more or less moisture-permeable. Alternatively, similarly watertight, two-component coatings have been used (epoxy resins, for example), sometimes mixed with a solvent and/or with charges of very fine fillers and dyes. In this case, polymerization occurs *in situ* due to the reaction between the two components, with the consequent formation of a thin layer that is as much adhesive to the masonry substrate and as much moisture-impermeable as the above.

In fact, the reason for many unsuccessful results is exactly the formation of a layer of polymeric material that is too impermeable to moisture [11]. If, on the one hand, the almost watertight coating protects the masonry against rain, on the other hand it prevents moisture inside masonries from evaporating towards the outside, or it allows it to occur very slowly. Consequently, ice formation in the masonry wall due to ambient cooling causes sharp swelling and spalling of rendering mortar. Alternatively, quick ambient heating when the masonry is exposed to the sun makes the vapour pressure inside the masonry increase with the consequent spalling of rendering mortar.\*

In addition to the above reasons, according to which polymeric coatings caused the falling of rendering mortars from the masonries of historical buildings, and also of recent constructions [17], the coating watertightness has also been one of the main causes of masonry deterioration. As a matter of fact, chemical degradation may occur only in the presence of moisture. Water has a double role: it acts as 'carrier' of water-soluble ions (sulphates and alkalis) towards the masonry components (amorphous silica, hydrated calcium silicates and aluminates) with which salts interact negatively; and it is one of the necessary components taking part in the course itself of deteriorating reactions (Section 3).

In Section 4.2 below we investigate the possible causes of deterioration due to interactions among original materials and the materials used later in restoration and consolidation works. It frequently occurs that, after the first period of apparent improvement due to the restoration and consolidation of masonries, historical buildings deteriorate even more severely than before the intervention.

\*Obviously, the formation of an almost impermeable layer of polymeric latex, epoxy resin, or even cement mortar with low water/cement ratio (therefore little porous), does not cause these problems if the masonry is absolutely and continuously dry, because the coating, in this case, protects the masonry against the action of rain or the environment.

#### 4.2 Deterioration, after restoration work, caused by the formation of ettringite and/or thaumasite

Apart from the unsuccessful use of polymeric materials, mainly due to the waterproofing of moist masonries, that was dealt with above, the present section investigates the causes of failure of restoration or consolidation works executed by the use of hydraulic binders, such as Portland cement, hydraulic lime or even lime-pozzolan mixtures.

In all these cases, the hydraulic ability of the binder (due to the formation of hydrated calcium aluminates and silicates) that promotes the water-resistance of hardened mortars is also responsible for possible interactions with calcium sulphate, which might be present in masonries because of one of the reasons explained in Section 4.1.1.2.

Fig. 5 shows schematically the reaction process that leads to the formation of ettringite. The following conditions are necessary in order that the reaction may occur:

- the presence of sulphates in the masonry;
- the presence of calcium aluminates in mortars used in the restoration work;
- the presence of moisture in the masonry.

Fig. 6 shows schematically the reaction process that leads to the formation of thaumasite. Also in this case, three conditions are necessary in order that the reaction may occur:

- the presence of sulphates in the masonry;
- the presence of hydrated calcium silicates in mortars used in the restoration work;
- the presence of moisture.

As shown in the reaction diagrams of Figs 5 and 6, when hydraulic mortar based on cement, hydraulic lime or even lime-pozzolan is used in restoration work, the formation of hydrated calcium aluminates and hydrated calcium silicates is possible. Therefore, if calcium sulphate and moisture are present in masonries, due to one of the reasons illustrated in Section 4.1.1.2, the possible consequence is the formation of ettringite (Fig. 5) and/or thaumasite (Fig. 6), resulting in more or less rapid deterioration of the restoration mortar.

In addition, if cement, or other hydraulic binders, are used to produce cement grouts for injection as consolidation of inside masonries, the production of ettringite and/or thaumasite may compromise also the statics of the building, when expansive and destructive phenomena involve masonries extensively.

The formation of ettringite may occur also when traditional air-hardening binders (lime and gypsum) are used, if given conditions are present in masonries to restore (Fig. 7). For example, ettringite may be formed when lime in the restoration mortar was used in masonries containing, as original materials, pozzolan and gypsum used as binder or coming from sulphate salts in bricks or from seawater flowing through capillaries

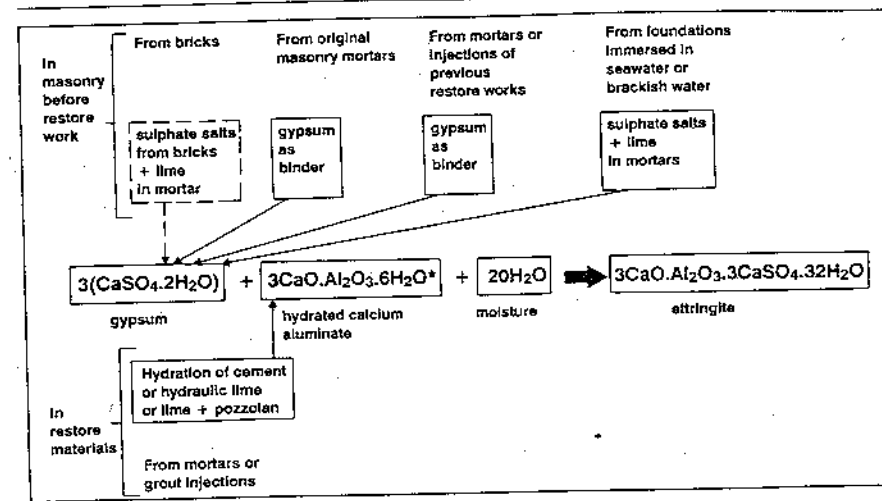


Fig. 5 Possible interactions between hydraulic binders used in restoration work and pre-existing sulphate in the masonry leading to the formation of ettringite. The part marked by an interrupted line relates only to bricks containing sulphate salts. \*This hydrated calcium aluminate can be substituted by the other hydrated calcium aluminates, e.g.  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ .

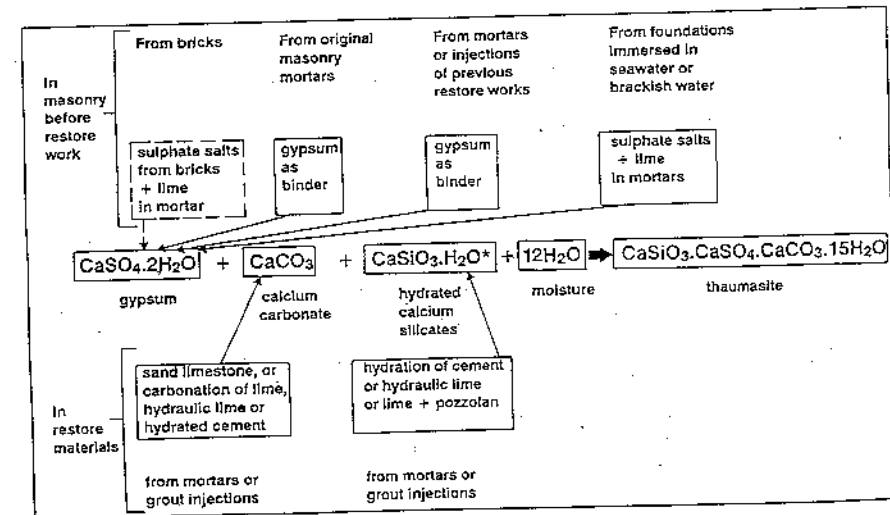


Fig. 6 Possible interactions between hydraulic binders used in restoration work and pre-existing sulphate in the masonry, leading to the formation of thaumasite. The part marked by an interrupted line relates only to bricks containing sulphate salts. \*This hydrated calcium silicate stands for hydrated calcium silicates with the generic formula  $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$  (C-S-H).

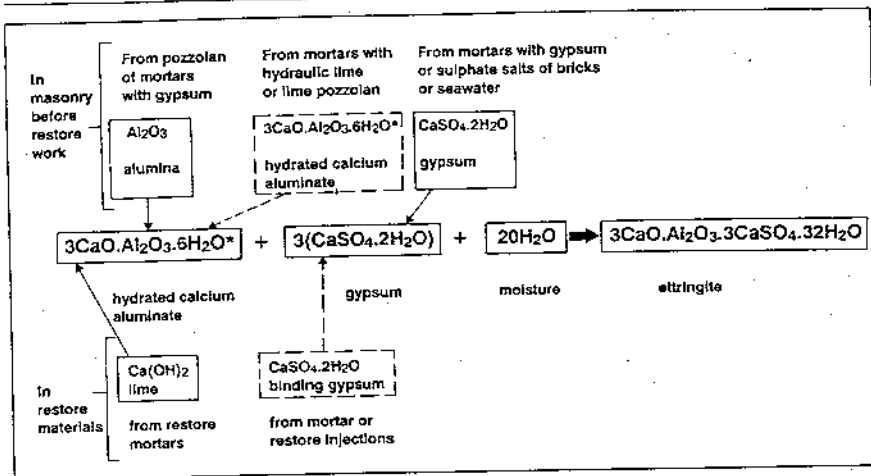


Fig. 7 Possible reactions between air-hardening binders (lime or gypsum) used in restoration work and hydrated calcium aluminates (either forming or pre-existing, respectively) in the masonry. The parts marked by interrupted lines relate to the production of ettringite when the binder of the restoration work is gypsum. Continuous lines refer to the production of ettringite when lime is used as binder in the restoration work. \*This hydrated calcium aluminate can be substituted by other hydrated calcium aluminates, e.g.  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ .

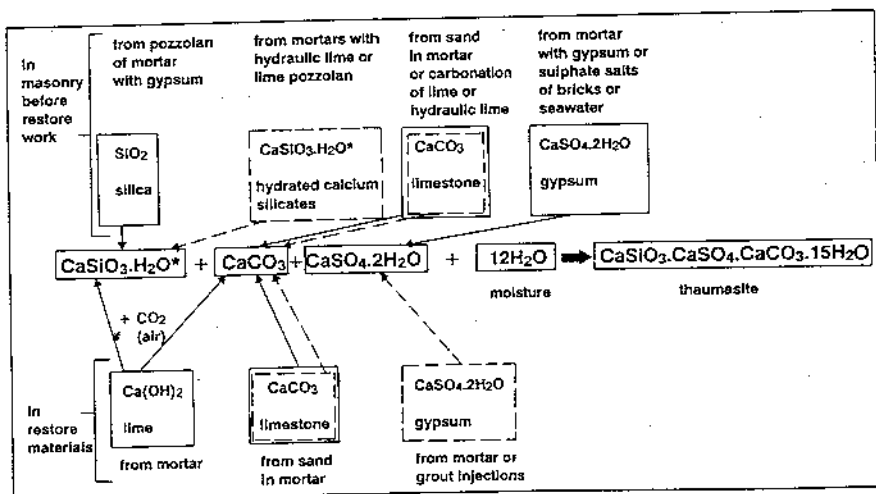


Fig. 8 Possible reactions between air-hardening binders (lime or gypsum) used in restoration work and hydrated calcium silicates (either forming or pre-existing, respectively) in the masonry. The parts marked by interrupted lines relate to the production of ettringite when the restoration binder is gypsum. Continuous lines refer to the production of thaumasite when the restoration binder is lime. \*This hydrated calcium silicate stands for hydrated calcium silicates with the generic formula  $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$  (C-S-H).

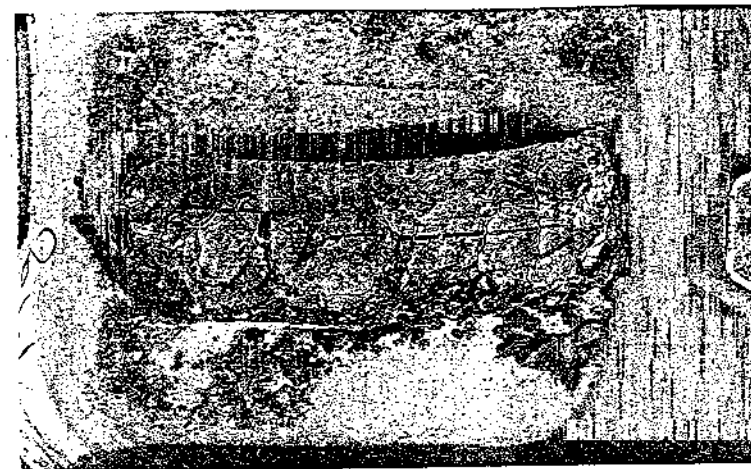


Fig. 9 Cement mortar specimen cracked owing to ettringite formation.

(Fig. 7, continuous lines). Ettringite may also form if gypsum in the restoration mortar is used in masonries containing hydrated calcium aluminates from mortars based on hydraulic lime or lime-pozzolan (Fig. 7, interrupted lines).

On the other hand, the formation of thaumasite may also occur when traditional air-hardening binders (lime and gypsum) are used, as illustrated in Fig. 8. Continuous lines indicate the reagents that lead to the formation of thaumasite when using lime in restoration work, whereas interrupted lines indicate the thaumasite formation when gypsum is used in the restoration mortar.

Whatever the scheme of the reactions leading to the formation of ettringite or thaumasite, according to Figs 5 to 8, the main differences between the two reactions are as follows:

(a) The formation of ettringite causes expansion in mortar but, even after cracking, the material is still sound and resistant. Conversely, thaumasite is not accompanied by significant expansion, but after its formation, mortar becomes incoherent and, without resistance, providing an incoherent mass particularly in the presence of water. The pictures in Figs 9 and 10 show a cracked laboratory specimen and a completely destroyed one, due to ettringite and thaumasite, respectively, formed by cement mortar in contact with a magnesium sulphate solution. The pictures in Figs 11 and 12 show two rendering mortars based on cement that deteriorated because of the formation of ettringite or thaumasite, respectively, both detected by X-ray diffraction analysis: in the first case, rendering mortar fell out, but it is still coherent; conversely, in the second case, a finger can penetrate the incoherent and non-

resisting mortar, because of the formation of thaumasite.

(b) Ettringite forms more rapidly than thaumasite, therefore the presence of thaumasite is very often preceded by the formation of ettringite [15]. Thaumasite may form in a few tens of days or in a few years' time, depending on ambient conditions (temperature, moisture, etc.).

(c) Although low temperatures favour the formation of both processes, in cold climates the formation of thaumasite is specially accelerated [12,15]: optimum thermo-hygrometric conditions for the formation of thaumasite are RH 90% and temperature ranging from 0 to 5°C.

Both ettringite and thaumasite are detectable by X-ray diffraction analysis, provided that specimens are moisturized if they have been taken from a masonry exposed to the sun and therefore possibly dry. As a matter of fact, excess drying might decompose ettringite and thaumasite and prevent X-rays from recognizing them, notwithstanding their real presence in the deteriorated masonry.

Physico-mechanical phenomena accompanying the formation of ettringite and thaumasite depend on the type of restoration work. In the case of cement grout injection to consolidate masonries, the increase in volume following the formation of ettringite can lead to the almost immediate cracking of the construction. Obviously, this depends on the amount of ettringite formed and on the tensile strength of the masonry to be consolidated. Conversely, if thaumasite forms, after an initial consolidation soon after the grout injection, the binding system loses its strength slowly and progressively, even causing the collapse of the structure.



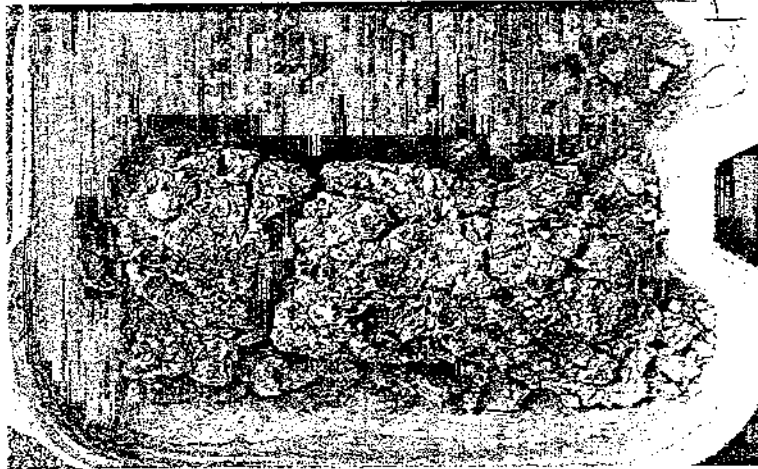


Fig. 10 Cement mortar specimen destroyed by thaumasite formation.



Fig. 11 Rendering mortar deteriorated due to the formation of ettringite. The mortar swells and falls out; however, residual rendering mortar is still coherent.

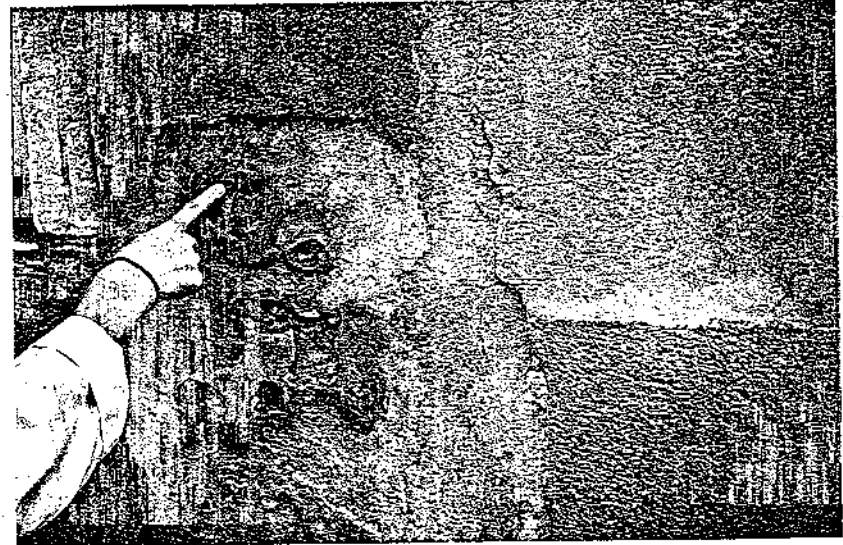


Fig. 12 Rendering mortar deteriorated due to the formation of thaumasite; the mortar is so incoherent that even a finger can easily penetrate.

When jointing or rendering mortars are repaired, the formation of ettringite is accompanied by mortar swelling, pop-outs and falling, while thaumasite causes mortar softening: since mortar can be leached easily by rain, it is not always possible to find thaumasite if the diagnostic intervention occurs long after deterioration.

#### 4.2.1 Brick masonry deterioration due to ettringite or thaumasite formation after restoration work

Table 5 shows again the 20 possible types of brick masonries according to the materials originally used. Masonries marked by \* refer to those repaired by hydraulic binders (cement, hydraulic lime, lime-pozzolan) interacting with pre-existing binding gypsum in the jointing mortar to form ettringite and/or thaumasite according to the reaction diagrams shown in Figs 5 and 6. This category comprises *Beg*, *Beg'*, *Bm<sub>gg</sub>*, *Bm<sub>gg</sub>'*, *Bm<sub>gl</sub>*, *Bm<sub>gl}'</sub>*, *Bm<sub>g'g</sub>*, *Bm<sub>g'g}'</sub>*, *Bm<sub>gl'g</sub>*, *Bm<sub>gl'g}'</sub>*. Obviously even masonries which are not marked by \* may fall into this category, if gypsum was used in previous restoration work.

Masonries originally containing gypsum as rendering mortar binder are marked by Δ. Therefore, if it has not been removed completely, residual gypsum can form ettringite and/or thaumasite (Figs 5 and 6) with the hydraulic binder used in the restoration work. Masonries *Bm<sub>gg</sub>*, *Bm<sub>g'g</sub>*, *Bm<sub>g'g}'</sub>*, *Bm<sub>gl'g</sub>*, *Bm<sub>gl'g}'</sub>*, *Bm<sub>l'g</sub>*, *Bm<sub>l'g}'</sub>* fall into this category.

Masonries marked by ○ in Table 5 can deteriorate if lime and ordinary sand (therefore non-hydraulic mortars) are used in the restoration work and the original masonry had been constructed by the use of pozzolanic sand in combination with gypsum (g'). The masonries *Beg'*, *Bm<sub>gg</sub>'*, *Bm<sub>g'g</sub>'*, *Bm<sub>gl'g</sub>'*, *Bm<sub>l'g</sub>'* fall into this category. The schemes leading to the formation of ettringite and thaumasite are indicated in Figs 7 and 8, respectively.

The masonries marked by ◇ in Table 5 can degrade if gypsum is used in the restoration work and the original masonry had been built by using lime-pozzolan or hydraulic lime mortar (Figs 7 and 8). The masonries *Bel'*, *Bm<sub>gl}'</sub>*, *Bm<sub>gl'g</sub>'*, *Bm<sub>l'g</sub>'*, *Bm<sub>l'g}'</sub>* fall into this category.

#### 4.2.2 Stone masonry deterioration due to ettringite or thaumasite formation after restoration work

Stone masonries deteriorating because of sulphate attack following restoration work are shown in Table 6. They are marked by the same symbols used in Table 5. The main difference between brick masonries and stone masonries is the content of water-soluble sulphates. Bricks can contain amounts of sulphates of such a value that they can cause the formation of ettringite and thaumasite, even in the absence of binding gypsum among original materials or sulphate waters wetting foundations.

Table 5 Brick masonry deterioration due to sulphate attack after restoration work

Joining mortar	Brick masonry exposed to view (Be)				Brick masonry with rendering mortar (Bm)			
	'Inside' binder: gypsum		'Inside' binder: lime		'Inside' binder: gypsum		'Inside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	Beg	Beg'	Bel	Bel'	Bmg	Bmg'	Bmg	Bmg'
	'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	Bmgg	Bmgg'	Bmgl	Bmgl'	Bmg'g	Bmg'g'	Bmg'l	Bmg'l'
	'Inside' binder: lime				Pozzolanic sand			
	Ordinary sand				Bml'			
	'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	Bmlg	Bmlg'	Bml'l	Bml'l'	Bml'g	Bml'g'	Bml'l	Bml'l'

\* Deteriorates if hydraulic binders are applied inside or on the masonry.  
 Δ Deteriorates if hydraulic binders are used in the repair work of the old gypsum rendering mortar whose residual parts are still present.  
 ◊ Deteriorates if binding gypsum is used inside or on the masonry originally containing hydraulic lime or lime and pozzolan whose residual parts are still present.  
 ◊ Deteriorates if lime is used inside or on the masonry originally containing gypsum and pozzolan whose residual parts are still present.  
 Note: In addition to masonries marked by \* Δ ◊ and ◊, deterioration after restoration work can also affect masonries without binding gypsum, but with bricks rich in sulphate salts or moisturized with sulphate waters (seawater) flowing through capillaries into the masonry.

Table 6 Stone masonry deterioration due to sulphate attack after restoration work\*

Joining mortar	Stone masonry exposed to view (Sc)				Stone masonry with rendering mortar (Sm)			
	'Inside' binder: gypsum		'Inside' binder: lime		'Inside' binder: gypsum		'Inside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	Seg	Seg'	Sc'l	Sc'l'	Smg	Smg'	Smg	Smg'
	'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	Smgg	Smgg'	Smgl	Smgl'	Smg'g	Smg'g'	Smg'l	Smg'l'
	'Inside' binder: lime				Pozzolanic sand			
	Ordinary sand				Sm'l'			
	'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	Sm'l	Sm'l'	Sm'l'l	Sm'l'l'	Sm'l'g	Sm'l'g'	Sm'l'l	Sm'l'l'

\* For key to symbols see Table 5.  
 Note: In addition to masonries marked by \* ◊ Δ and ◊, deterioration after restoration work can also affect masonries without binding gypsum, but with stones moisturized with sulphate waters (seawater) flowing through capillaries into the masonry.

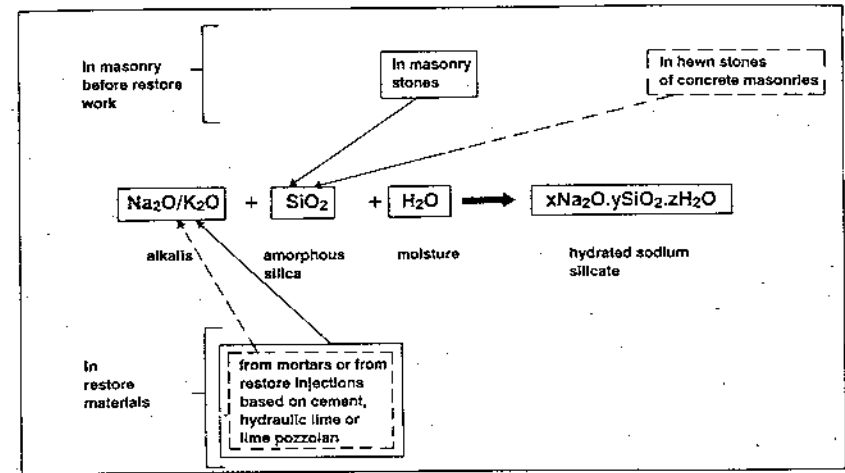


Fig. 13 Possible interactions between hydraulic binders used in restoration work and amorphous silica of stone masonries (continuous line) or concrete masonries (interrupted line) due to alkali-amorphous silica reaction.

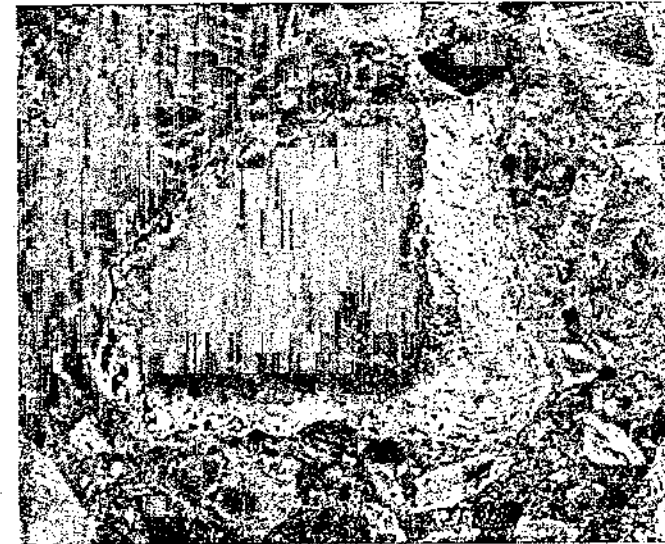


Fig. 14 Amorphous silica grain surrounded by hydrated sodium silicate formation (pale regions).

Table 7 Concrete masonry deterioration due to sulphate attack after restoration work\*

Concrete masonry exposed to view (Ce)		Concrete masonry with rendering mortar (Cm)								
'Inside' mortar	'Inside' binder: lime	'Inside' binder: lime								
	Ordin. sand, hewn stone	Pozzol. sand, hewn stone	Ordinary sand, hewn stone		Pozzolanic sand, hewn stone					
	Cel	◇ Cel'	Cml		Cml'					
Rendering mortar			'Outside' binder: gypsum		'Outside' binder: lime		'Outside' binder: gypsum		'Outside' binder: lime	
	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand	Ordin. sand	Pozzol. sand
	△ Cmlg	c Cmlg'	Cml	◇ Cml'	△◇ Cml'g	△◇○ Cml'g'	◇ Cml'i	◇ Cml'l'		

\*For key to symbols see Table 5.

The degradation mechanism is the same as that shown in Figs 5 and 6, if hydraulic binders (cement, hydraulic lime, lime-pozzolan) are used in the restoration work, and this is illustrated in Figs 7 and 8, if air-hardening binders (lime and gypsum) are employed in the restoration work.

#### 4.2.3 Concrete masonry deterioration due to ettringite and thaumasite formation after restoration work

Table 7 shows concrete masonry deterioration due to sulphate attack as a consequence of restoration work executed by hydraulic binders, according to the mechanism indicated in Figs 5 and 6 and by air-hardening binders, according to the mechanism illustrated in Figs 7 and 8.

#### 4.3 Degradation caused by alkali-stone reaction after the restoration work of stone and concrete masonries

It is known, from the chemistry of concrete [18], that cement alkalis can react with a number of amorphous silicas present in aggregates to produce very voluminous products (hydrated sodium or potassium silicates) (Fig. 13). The reaction is accompanied by expansive, disruptive phenomena on the slab or wall surface (pop-outs) or it may involve the whole structure, causing cracking.

In this case, as in sulphate attack, the presence of moisture inside the masonry, even occurring discontinuously, is a necessary condition. If the stones of the masonry contain amorphous silica (opal, chalcedony) or badly crystallized forms of cristobalite and tridymite, the reaction shown in Fig. 13 may occur when binders

employed in the restoration work are relatively rich in alkalis (more than 0.60% if expressed as  $\text{Na}_2\text{O}$ ).

The diagnostic solution is not easy, compared with the relatively simple problem of sulphate attack. The final products of the reaction, unlike ettringite and thaumasite, cannot be identified easily and immediately through X-ray diffraction analysis, due to the lack of crystallinity of the alkali-aggregate reaction product. However, petrographic inspection as shown in Fig. 14 allows the formation of alkaline hydrated silicates (pale regions) at the interface between the reactive grain (centre) and the surrounding cement matrix to be shown clearly.

## 5. CONCLUSION

The recovery of historical buildings is a very delicate operation, since the materials employed in restoration work can interact negatively with some of the compounds that might be present in masonries.

Owing to these reactions, the restoration operation can worsen the state of masonries. These reactions cause swelling, pop-out and falling of jointing and rendering mortars applied during the restoration work, as well as of cement grout injections for inside consolidation of structures.

## REFERENCES

1. Ludwig, U. and Mehr, S., 'Destruction of historical buildings by the formation of ettringite or thaumasite', in Proceedings of 8th International Congress on the Chemistry of Cement, Rio de Janeiro, 1986, Vol. V, p. 181.

2. Colleparidi, M., 'Scienza e Tecnologia del Calcestruzzo', 2nd Edn (Hoepli, Milano, 1987).
3. Goria, C., 'Evoluzione storica dei leganti e dei conglomerati: dall'empirismo alla loro conoscenza razionale', in 'Cemento: Storia, Tecnologia, Applicazioni' (Fratelli Fabbri Editori, Milano, 1976).
4. Lea, F. M., 'The Chemistry of Cement and Concrete' (Chemical Publishing, London, 1971).
5. Palladio, A., 'Trattato di Architettura. Libri 4', (Venezia, 1570).
6. Momo, M., 'Note su produzione ed uso delle malte di calce nella prima metà del Settecento', in 'Atti del Seminario Rilem, Le malte nell'evoluzione del processo costruttivo: passato, presente, futuro', edited by Anna Gilbert (Volterrani, Torino, 1988) p. 53.
7. Colleparidi, M., 'Materiali inorganici da costruzione', in 'Enciclopedia della Chimica' (Isedi, Milano, 1977).
8. Cussino, L., 'Le malte oggi: materiali in produzione', in 'Atti del Seminario Rilem, Le malte nell'evoluzione del processo costruttivo: passato, presente, futuro', edited by Anna Gilbert (Volterrani, Torino, 1988) p. 45.
9. Emiliani, T., 'La Tecnologia della Ceramica' (Fratelli Lega, Faenza, 1957).
10. Adam, J. P., 'La construction romaine. Matériaux et techniques' (Picard, Paris, 1984).
11. Furlan, V., in Atti del Convegno 'Intonaci Colore e Coloriture nell'Edilizia Storica', Roma, 1984, Bollettino d'Arte, Supplemento, Vol. I (Ministero dei Beni Culturali ed Ambientali) p. 95.
12. Lachaud, R., 'Thaumasite et ettringite dans les matériaux de construction', *Ann. Inst. Techn. Bâtiment Trav. Publ.* 370 (1979) 3.
13. Mehta, P. K., 'Mechanism of expansion associated with ettringite formation' *Cem. Concr. Res.* 3 (1973) 1.
14. Colleparidi, M., 'Scienza e Tecnologia del Calcestruzzo', 2nd Edn (Hoepli, Milano, 1987) p. 227.
15. Crammond, N. J., 'Thaumasite in failed cement mortars and renders from exposed brickwork', *Cem. Concr. Res.* 15 (1985) 1039.
16. Colleparidi, M., 'Scienza e Tecnologia del Calcestruzzo', 2nd Edn (Hoepli, Milano, 1987) p. 7.
17. Furlan, V. and Kohler, N., 'Dégradation prématurée des enduits à base de résine synthétique', in 'Chantiers 8' (1981) p. 13.
18. Colleparidi, M., 'Scienza e Tecnologia del Calcestruzzo', 2nd Edn (Hoepli, Milano, 1987) p. 277.

## RÉSUMÉ

### Dégradation et restauration des maçonneries de constructions historiques

On a tenté d'établir une classification des murs de maçonnerie en tenant compte de toutes les combinaisons possibles de matériaux d'origine qui se rencontrent dans les constructions historiques: chaux, plâtre, chaux hydraulique, pierre, brique, etc. Sur cette base on a pris en compte 50 murs de maçonnerie virtuels de constructions historiques.

On a analysé les causes possibles de détérioration chimique des maçonneries dues aux interactions entre les matériaux d'origine: les raisons potentielles de dégradation chimique sont fondamentalement liées à la réaction alcaline de la silice amorphe (dans les pierres) et tout particulièrement aux réactions des sels de sulfates qui déterminent la formation d'ettringite et/ou de thaumasite.

Dans les deux cas, l'eau joue un rôle essentiel dans le déroulement des réactions que nous venons de mentionner: c'est seulement en présence d'humidité - même occasionnelle - que les maçonneries de constructions historiques ont subi une détérioration significative.

La rénovation des constructions historiques est une opération très délicate, car il peut se produire une interaction négative entre les matériaux employés dans les travaux de restauration et certains des composants présents dans les maçonneries; pour cette raison, l'opération de restauration peut aggraver l'état des maçonneries. Ces réactions déterminent gonflement, cratères et effritement des mortiers de jointoiement et de revêtement appliqués pendant le travail de restauration, comme pendant les injections de coulis de ciment pour la consolidation interne des structures. De nouveau, on peut constater l'action défavorable de l'ettringite et/ou de la thaumasite en présence d'humidité les maçonneries dans des constructions.