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Thaumasite formation and deterioration in historic buildings

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Abstract

Thaumasite and ettringite can be found among the deterioration products of cementitious materials exposed to sulphate attack. This can occur in concrete structures, as well as in masonry walls of historic buildings erected before the advent of Portland cement. Masonry walls of historic buildings may contain gypsum or other sulphate salts for different reasons. When they need to be repaired, C-S-H and C-A-H, formed by the hydration of hydraulic binders used for restoration, can react with water and gypsum or sulphate salts and produce thaumasite and ettringite. Due to these reactions, degradations of the repaired historic buildings can occur causing expansion, cracking, spalling and strength loss. In order to assess preliminarily the chemical compatibility of a repairing cementitious material with the presence of gypsum or sulphate salts inside historic buildings, the Anstett test can be adopted. Alternatively, protection measurements, based on the hindrance of water to penetrate the walls, should be adopted since in the absence of water both thaumasite and ettringite cannot be produced, even in the presence of gypsum, or other sulphate salts inside the historic buildings. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ettringite; Historic buildings; Hydraulic binders; Sulphate attack; Thaumasite

1. Introduction

Thaumasite and ettringite are two substances which are found among the deterioration products of cementitious materials exposed to sulphate attack. This can occur in concrete structures [1–4] as well as in masonry walls of historic buildings [5–7].

Ettringite's composition ($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$) indicates that it may form by the reaction of water with calcium sulphate and the alumina-bearing hydration products ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$, $3CaO{\cdot}Al_2O_3\ {\cdot}6H_2O$, $C_3A{\cdot}CaSO_4{\cdot}12\text{-}18H_2O$, etc.). These products, sometimes also indicated as C-A-H, form by hydration of Portland cement or other binders, such as hydraulic lime or mixtures of lime and pozzolan [8,9].

Thaumasite ($CaCO_3{\cdot}CaSO_4{\cdot}CaSiO_3{\cdot}15H_2O$) may form by the reaction of water with calcium carbonate, calcium sulphate and hydrated calcium silicates which, again, are present in concrete or mortar mixtures, containing Portland cement, hydraulic lime or lime–pozzolan mixtures as binders [8,9]. The composition of hydrated calcium silicates, which may vary within a relatively wide range, is indicated by the generic formula xCaO·ySiO$_2$·zH$_2$O or C-S-H for short.

In general, Portland cement or Portland-based blended cements have been used in concrete mixes. However, before the advent of Portland cement at the end of the 19th century, gypsum, lime, lime–pozzolan mixtures and hydraulic lime — a sort of precursor of Portland cement — were widely used for jointing or rendering mortars or even for concrete mixtures of masonry walls of historic buildings. Moreover, Portland cement has been widely used to repair the damaged masonry walls of historic buildings, and therefore it will be taken into account as one of the cementitious materials which is present in this type of building.

Except when lime — $Ca(OH)_2$ — and plaster of Paris — $CaSO_4{\cdot}1/2H_2O$ — or a combination of these binders were used for historic buildings, in all other cementitious materials silica and alumina were available to produce C-S-H and C-A-H, respectively, as hydration products [8].

Calcium hydroxide was also present as a hydration product from Portland cement or as the original material in hydraulic lime or lime–pozzolan mixtures. Because of the exposure to air, $Ca(OH)_2$ was partly or totally transformed into $CaCO_3$. Therefore all the ingredients (C-S-H, C-A-H and $CaCO_3$) are available in the cementitious materials of historic buildings to produce thaumasite and/or ettringite when exposed to the action of water and gypsum.

Figure 1 schematically shows the chemical process for the hydration of anhydrous cementitious materials (hydraulic lime, lime–pozzolan mixture, Portland

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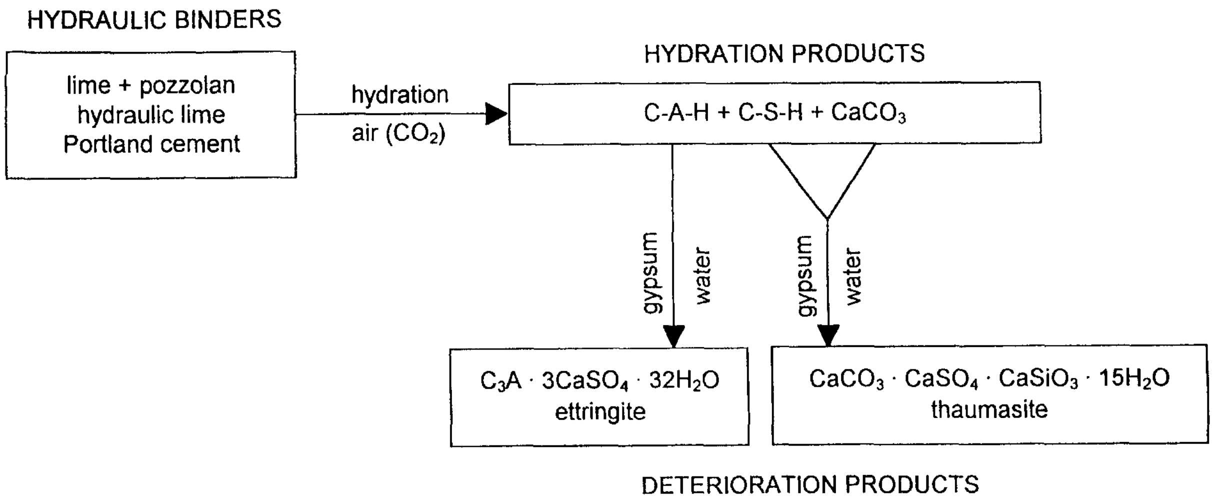

Fig. 1. Schematic process of thaumasite and ettringite formation by sulphate attack on cementitious hydration products.

cement) and then the reaction of the hydration products (C-S-H, C-A-H, $CaCO_3$) with water and gypsum ($CaSO_4 \cdot 2H_2O$), to produce thaumasite and ettringite.

However, this process — based on chemical change only — is not able to answer the following questions:

- why do ettringite and thaumasite cause deterioration of mortars and concrete in historic buildings?
- what is the relationship between ettringite and thaumasite?
- where do water and gypsum come from in historic buildings?
- how to repair historic buildings without the risk of thaumasite and/or ettringite deterioration?

In the following sections the author will attempt to answer these questions.

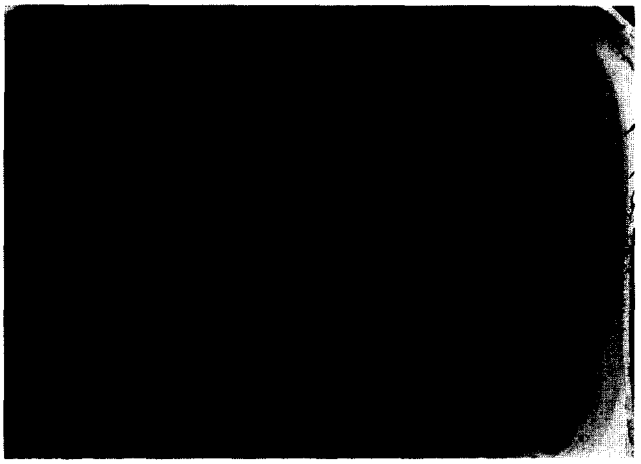

Fig. 2. Laboratory mortar specimen deteriorated by ettringite formation.

2. Deterioration caused by ettringite and thaumasite

Formation of thaumasite and ettringite occurs in several forms including expansion, cracking, spalling, loss of strength and adhesion. Ettringite formation is, in general, associated primarily with expansion, cracking and spalling. On the other hand, thaumasite formation is accompanied by a more severe damaging effect which is able to transform hardened concretes or mortars in a pulpy mass because of the loss of strength.

Figure 2 shows a laboratory mortar prism where ettringite production was caused by immersion in a calcium sulphate aqueous solution: differential expansion (due to the initial transformation of C-A-H into ettringite only on the outside layer of the prism) produced cracking and curling. Figure 3 shows cracking and spalling in a lime–pozzolan rendering mortar of an historic building caused by ettringite formation.

According to Mehta [10] the physical mechanism by which ettringite causes expansion and cracking is based

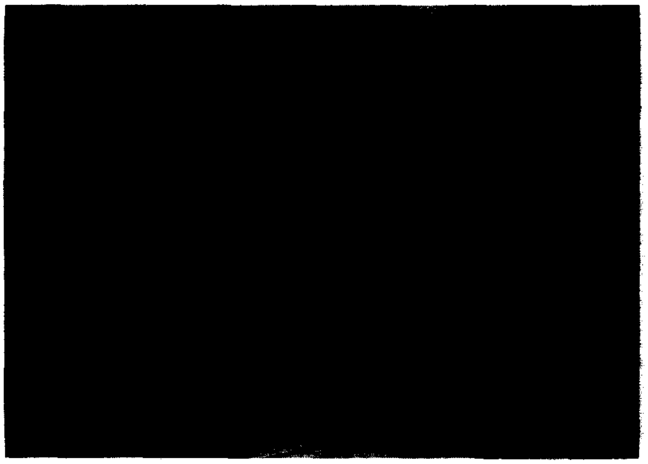

Fig. 3. Deterioration of lime–pozzolan rendering mortar of historic building caused by ettringite formation.

on swelling of ettringite by water adsorption and on topochemical formation of ettringite with directional crystal growth. However, these mechanisms alone cannot explain the loss of strength and adhesion which always accompanies sulphate attack. Mehta thinks that some strength loss occurs before ettringite forms and swells due to water adsorption. When sulphate sources other than calcium sulphate are available — for instance, sodium, potassium or magnesium salts — gypsum forms by consuming Ca^{+2} from both $Ca(OH)_2$ and C-S-H. Therefore, gypsum formation would be accompanied by decomposition of $Ca(OH)_2$ and C-S-H. Since C-S-H is the primary source of strength, the reduction in C-S-H, rather than gypsum formation itself, would be responsible for the strength loss accompanying the sulphate attack. However, this strength loss mechanism, based on gypsum formation and C-S-H decomposition, cannot work when ettringite forms and calcium sulphate is the salt initially available for sulphate attack. In other words, when ettringite forms without preliminary gypsum formation, no strength loss should occur since C-S-H is not consumed.

On the other hand, thaumasite formation consumes C-S-H independently of the type of sulphate salt. Figure 4 shows the dramatic change produced by thaumasite formation in a laboratory mortar prism in contact with a calcium sulphate aqueous solution. Because of the conversion of C-S-H and $CaCO_3$ to thaumasite, a significant strength loss was registered and the specimen was completely destroyed. Since C-S-H has been consumed in thaumasite formation, this process produces significant strength loss, even in the absence of a preliminary gypsum formation process.

Figure 5 shows a typical incoherent rendering mortar where thaumasite formed: due to the loss of strength, the mortar became so soft that even a finger could easily remove it.

Fig. 4. Laboratory mortar specimen destroyed by thaumasite formation.

Fig. 5. Strength loss of a lime–pozzolan rendering mortar caused by thaumasite formation.

Thaumasite and/or ettringite can also form in concrete walls. For instance, in the structure shown in Fig. 6 a lime–pozzolan mortar mixture was placed between two used as permanent formworks. Then crushed stones and bricks were pushed in by hand into the fresh mortar. Again, C-S-H and C-A-H are available in the hardened concrete and they can react with water and gypsum, if any, to produce thaumasite and ettringite, respectively, according to the process shown in Fig. 1.

3. Relationship between ettringite and thaumasite

In spite of the difference between ettringite and thaumasite for the raw chemical composition

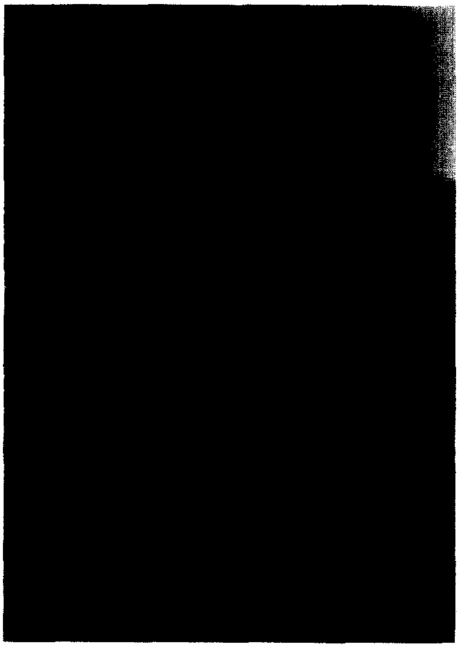

Fig. 6. Concrete wall found in Pompei, Italy.

($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ and $CaCO_3{\cdot}CaSiO_3{\cdot}CaSO_4{\cdot}15H_2O$, respectively) the crystallographic structure is very similar:

$Ca_6[Al(OH)_6]_2{\cdot}24H_2O\ [(SO_4)_3{\cdot}2H_2O]$ ettringite

$Ca_6[Si(OH)_6]_2{\cdot}24H_2O\ [(SO_4)_2{\cdot}(CO_3)_2]$ thaumasite

The Al^{+3} cation in ettringite is replaced by the Si^{+4} cation in thaumasite and this changes the number and the type of anionic groups ($SO_4^{-2}+CO_3^{-2}$ instead of SO_4^{-2} alone) to compensate the electrostatic charge of the cationic group.

Since the crystallographic structure of thaumasite and that of ettringite are closely related, the corresponding X-ray diffraction patterns are very similar (Fig. 7) particularly for the low angle–high intensity lines:

Thaumasite		Ettringite	
2θ Cukα	Intensity	2θ Cukα	Intensity
9.15	100	9.08	100
16.00	45	15.75	80
32.98	35	32.25	40

When thaumasite is present in small amounts and the high angle-low intensity lines are overlapped by the lines from other cementitious products, low angle–high intensity lines only can be used. In such a case, high resolution X-ray equipment is required to separate the lines of thaumasite and ettringite.

In order to improve the identification of small amounts of thaumasite in the presence of larger quantities of ettringite, the sample can be treated with a 5% Na_2CO_3 aqueous solution before X-ray diffraction (XRD) analysis [1]: ettringite and gypsum are completely removed by this treatment and the low angle–high intensity lines of thaumasite only are retained on the XRD pattern.

Both ettringite and thaumasite may not be identified by XRD analysis when thermo-hygrometrical drying in situ (i.e. on the masonry walls of historic buildings) causes partial or total decomposition of these products [11]. Rewetting for one week of the ettringite at 20°C and of the thaumasite at 4°C before the XRD analysis favours the intensity increase of the X-ray lines of these products [11].

Thaumasite in the form of fine needle crystal may be observed by scanning electron microscopy [12] and confirmed by chemical microanalysis indicating the presence of Ca, Si, O and S elements.

Other techniques — including thermal analysis [13], nuclear magnetic resonance [14], infrared and Raman spectroscopy [15,16] and optical microscopy [3] — offer additional means to identify thaumasite as a separate phase other than ettringite.

Thaumasite and ettringite have isomorphous crystal lattices and there are several papers indicating that these products are the end members of the solid solution series with carbonate ions replacing sulphate or hydroxyl ions of ettringite. Many authors think that thaumasite formation follows ettringite formation. For instance, Lachaud [4] prepared a mixture of alite, gypsum and calcite and found thaumasite at temperatures below 20°C only when alite contained some alumina; no thaumasite was found when an alumina-free alite was used.

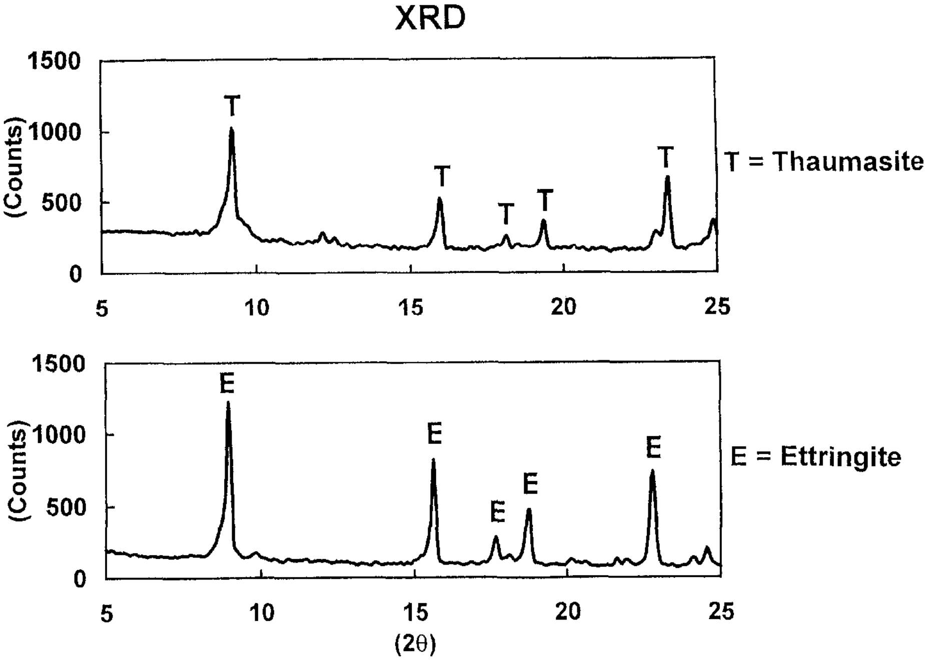

Fig. 7. Thaumasite and ettringite XRD patterns.

However, Ludwig and Mehr [5] were able to detect thaumasite formation — accompanied by a surface desintegration of the specimens — even when pure alumina-free alite was mixed with gypsum and calcite and stored under water at 2°C for at least 90 days; no sulphate attack, related to thaumasite formation, was recorded in the corresponding specimens at 20°C.

It seems that thaumasite formation can occur in field cases only at temperatures lower than room temperature. However, there is evidence that thaumasite formation accompanied by severe breakdown of mortar specimens can occur in laboratory tests at temperatures as high as 23°C [17]. On the other hand, Pauri and Collepardi [11] found that a thaumasite sample (taken from an historic building where low temperatures prevailed at the site) was stable when stored at 40°C; only at temperatures as high as 60°C did thaumasite decomposition occur, particularly at low relative humidities ($<35\%$). According to Knudsen [17] these data favour the point of view that the lack of formation of thaumasite at temperatures higher than room temperature is due to kinetic hindrance rather than a thermodynamic cause. This can explain why the author of the present paper was able to find thaumasite, even in historic buildings in the South Italy where the prevailing temperatures were higher than 20°C.

All the above data seem to confirm that thaumasite is stable, even in the absence of alumina and at temperatures higher than room temperature. However, an alumina impurity and lower temperatures seem to accelerate the process of thaumasite formation, particularly when preliminary ettringite is formed. Therefore, since in historic buildings (with mortars manufactured by hydraulic lime or lime–pozzolan mixtures and repaired by Portland cement-based mortars) both C-S-H and C-A-H are present, thaumasite and ettringite can be formed, provided that gypsum and water are available (Fig. 1).

4. Source of water and gypsum in historic buildings

Water is always present in historic buildings, with the exception of those in deserts and permanently dry areas. In particular, for historic buildings in Europe, water can come from two different sources: rain water or capillary rising water from the foundations in contact with wet grounds. In general, only the exterior of walls gets wet due to rain water, whereas both the exterior and the interior of walls are involved by capillary rising water. When water cannot escape because of an impermeable layer covering the wall, the theoretical rise can be as high as 15 m with capillary pore size of approx. 1 μm. Fortunately, due to the water evaporation, which occurs during the dry weather periods, the capillary rise is at most approx. 2 m in walls with a porous mortar rendering layer or without a rendering mortar. For instance, even in historic buildings permanently exposed to the capillary rise water as in Venice, the moisture suddenly decreases from the ground floor (about 15–20%) to the first floor (3–4%). Figure 8 schematically shows the capillary rise of water in walls of historic buildings with an impermeable layer on both the exterior and the interior side (A), an impermeable layer on the exterior side only (B), and without an impermeable layer on both sides (C).

Besides water, gypsum is needed to form thaumasite as well as ettringite (Fig. 1). Gypsum can be present in historic buildings for one of the following reasons:

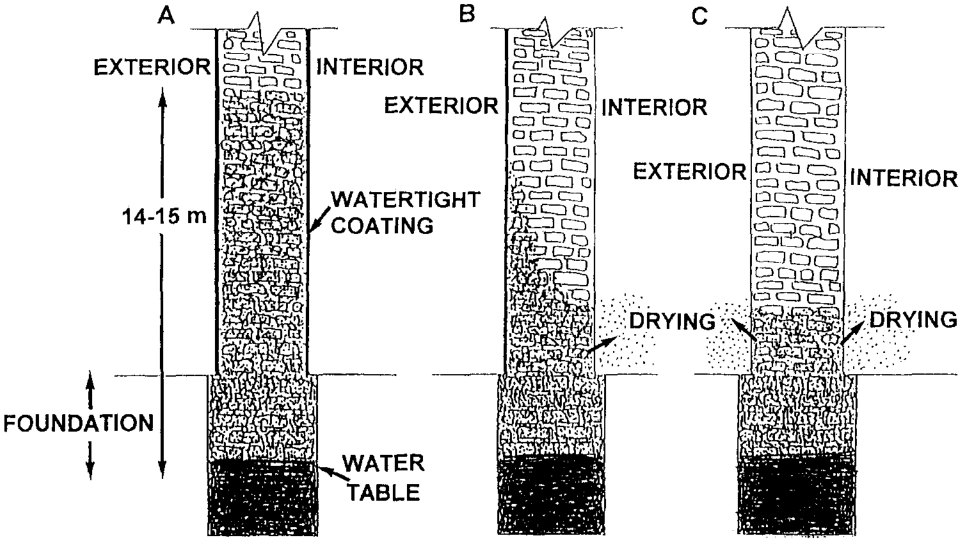

Fig. 8. Capillary rise of water in walls of historic buildings with an impermeable layer on both exterior and interior side (A), with an impermeable layer on the exterior side only (B), and without an impermable layer on both sides (C).

- it was used as binder for gypsum mortars in the original construction [5,7,18] or in the later repair of the buildings [5,7];
- it could form by the reaction of sodium or magnesium sulphate from bricks with lime or C-S-H in jointing or rendering mortars [7];
- it could form in situ by reaction of SO_2 (in polluted environments of urban and industrial areas) with oxygen, water and lime or calcite of the surface mortar [19];
- it could form by reaction of sulphate ions in capillary rise water (particularly seawater as in Venice) with lime or C-S-H of the cementitious materials in the wall.

When gypsum formed by one of the above in situ reactions, liquid water played the important role of carrying one component (for instance SO_4^{2-}) towards the other (for instance Ca^{2+}) due to its random movement inside the masonry walls caused by capillary rise or rain water penetration and subsequent drying. Figure 9 shows severe cracking caused by thaumasite and ettringite formation in a stone wall of a historic building. A cement grout was injected to consolidate the wall where gypsum was used previously. Due to rain water as well as to capillary rise water, thaumasite and ettringite formed after 1 year of the incorporation of cement grouting.

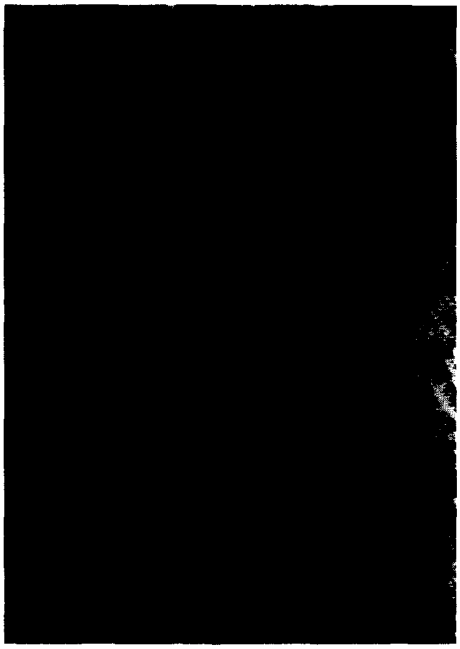

Fig. 9. Stone wall cracked by thaumasite and ettringite formation after consolidation with cement grouting.

5. Repair of historic buildings without thaumasite/ettringite deterioration risk

Portland cement mortars have been used to repair the outer shell of masonry walls or Portland cement grouts have been injected to consolidate the inner core of thick walls in historic buildings [5,7]. When gypsum is available for one of the reasons examined in the previous section, thaumasite and/or ettringite can form according to the process shown in Fig. 1. The replacement of Portland cement by hydraulic lime or lime–pozzolan mixtures does not exclude the presence of C-S-H and C-A-H as hydrated cementitious products and their subsequent conversion to thaumasite and ettringite when gypsum is available (Fig. 1).

However, not necessarily any type of hydraulic binder is capable to produce the C-S-H needed to produce thaumasite or C-A-H with the chemical composition required for ettringite formation. For instance, the CaO/SiO_2 molar ratio of the C-S-H phase to feed the production of thaumasite should be 1:1, whereas the CaO/Al_2O_3 molar ratio of the C-A-H to feed the ettringite formation should be 1:3. In general, the risk of thaumasite and ettringite formation is higher when ordinary Portland cement is used to repair historic building containing gypsum. This risk is expected to be lower when low C_3A or C_3A-free Portland cement are used, since these materials are supposed to be 'sulphate-resisting' cements. However, these cements contain a lot of ferrite phase (C_4AF) that may be an alternative source of ettringite in the form of $C_3(A,F)\cdot 3CaSO_4\cdot 32H_2O$. Moreover, these cements might be particularly vulnerable to thaumasite formation for the reaction of gypsum with C-S-H and $CaCO_3$.

The risk of thaumasite and/or ettringite formation when hydraulic lime is used as a repairing material is strongly dependent on the chemical composition of the binder. In the case of lime–pozzolan mixtures, the risk depends on the SiO_2 and Al_2O_3 contents of the pozzolan and the proportion of the ingredients.

In any case, it is not easy to predict the long-term behaviour of the cementitious repair material, in terms of thaumasite–ettringite formation, on the basis of its chemical composition only. A better approach to assess preliminarily the compatibility of a repairing cementitious material with the presence of gypsum, if any, inside historic buildings is based on the Anstett test [8,20]. According to this test the binder is mixed to a plastic paste with 50% water by mass. The paste is allowed to harden for 2 weeks, and then crushed to 5 mm size. The material is dried at 40°C, mixed with gypsum (50% by mass of the dried binder paste) and ground to zero residue on the 900 mesh sieve. The ground material is gauged with 6% water, filled into a

Fig. 10. Change in volume caused by thaumasite and ettringite formation of a cylindrical specimen in the Anstett test.

cylindrical mould (80 mm diameter, 30 mm high) and compressed under pressure (2 MPa) for 1 min. The cylindrical specimen is placed on filter paper, kept damp by letting the ends dip in water, and covered with a glass plate to form an airtight joint. The diameter change is measured up to 90 days and should not exceed 1.25%. Figure 10 shows the volume change in the cylindrical specimen caused by ettringite and thaumasite formation due to the presence of C-S-H and C-A-H in the hydrated binder.

This test is very severe because it exposes the binder to an amount of gypsum (50% by mass of the binder paste) rather different from practice. However, a binder which does not cause an expansion exceeding 1.25% according to this test can be considered to be a good candidate to repair historic buildings containing sulphate salts.

Additional or alternative protection measurements, which should be adopted to prevent thaumasite–ettringite formation when cementitious materials are used to repair historic buildings containing sulphate salts, are based substantially on the hindrance of water to penetrate the walls. In the permanent absence of water, ettringite or thaumasite cannot form even in the presence of gypsum in contact with C-A-H or C-S-H, respectively (Fig. 1). The following techniques are employed to block water from entering the walls:

- surface treatment of the walls by hydrophobic products, such as silane, to hinder the absorption of rain water; this treatment allows the inside water to escape in the form of vapor, since the pores of the masonry walls are not obstructed by silane treatment;
- cutting of the walls at ground level and insertion of a metallic or polymeric sheet to block the capillary rise of water; alternatively an epoxy grouting (to produce a mechanical barrier) or silane injection (to give a hydrophobic character to the inside wall) can be used to block the capillary rise water.

6. Conclusions

Historic buildings may contain gypsum or other sulphate salts for different reasons. When they need to be repaired, C-S-H and C-A-H, formed by the hydration of hydraulic binders used for the restoration, can react with water and gypsum and produce thaumasite and/or ettringite. Due to the formation of these products, degradation of the repaired structures can occur causing expansion cracking, spalling and strength loss.

In order to avoid this deterioration process, sulphate-resisting binders should be adopted for the restoration of historic buildings, so that thaumasite and ettringite do not form, even in the presence of water and gypsum.

Moreover, since in the absence of water both thaumasite and ettringite cannot be produced, additional or alternative measurements to hinder the deterioration of repaired historic buildings are based on the permanent drying of walls through mechanical and/or chemical treatments.

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