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Thaumasite formation due to atmospheric SO_2–hydraulic mortar interaction

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Abstract

The objective of this paper was to reproduce the formation of thaumasite due to the reaction of atmospheric SO_2 with hydraulic mortars. The research was carried out on mortars made with ordinary Portland cement (OPC), mineralized white Portland cement, hydraulic lime and a mixture of lime and pozzolana. Mortars underwent sulfation by exposing the samples to 300 ppm SO_2 at 25 °C and 95% RH for 2 days. Subsequently, half of the sulfated samples were kept for 6 and 12 months in a chamber with 0.3 ppm, SO_2 as pollutant (0.50 $\mathrm{l\,min^{-1}}$ flow gas velocity), 5 °C and 95% RH. The other halves of the sulfated samples were kept partially immersed in water at 5 °C for 4, 9 and 14 months.

The process of thaumasite formation in hydraulic mortars due to the interaction of the material with atmospheric SO_2 was reproduced in all the hydraulic mortars kept partially immersed in water at low temperature, except in the lime–pozzolana mixture. Gypsum was the first reaction product formed as a result of that interaction. Subsequently, gypsum reacted with calcium carbonate and C–S–H gel resulting in the formation of thaumasite. The formation of thaumasite was easier and quicker in sulfated samples kept at low temperature partially immersed in water. Only in OPC mortars was thaumasite formation observed in samples exposed to 0.3 ppm of SO_2 for 12 months.

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Keywords: Thaumasite; Durability; Sulfate attack; Hydraulic mortar

1. Introduction

The sulfation of mortars and concretes is a function of diverse environmental conditions; among those it is necessary to highlight SO_2 and aerosol concentration in the air, temperature, relative humidity, speed of the wind and presence of liquid water. It also depends on the characteristics of the material, including their chemical and mineralogical composition, porosity and permeability [1].

Phases from hydraulic mortar pastes can react in a different way with atmospheric SO_2 and consequently diverse compounds can be formed including calcium sulfite hydrate, gypsum, and syngenite [2,3]. One of the phases that could be formed as a consequence of the sulfation of the hydraulic binder is thaumasite. Obviously this phase cannot be formed by direct interaction between the SO_2 and the material; a series of intermediate stages (SO_2 solution in water filling the pores of material, SO_2 oxidation, H_2SO_3 and H_2SO_4 acids formation, etc.) should occur. As a consequence of the reaction among the previously mentioned acids and the binders, the conditions of precipitation of the thaumasite could be achieved. In the literature no data exist on the formation of thaumasite being atmospheric SO_2 the source of sulfation.

The main objectives of this work is to study the evolution of carbonated hydraulic mortars when they are exposed to an atmosphere containing SO_2 and to reproduce the formation of thaumasite through atmospheric SO_2–hydraulic mortars interaction, by mean of simulation tests carried out on mortars into a laboratory exposure chamber.

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2. Experimental

2.1. Mortar samples preparation

Mortar specimens for the simulation chamber tests were prepared using four different binders: hydraulic lime, lime and pozzolana, ordinary Portland cement (low in Al) and mineralized white Portland cement [10], together with sand. Up to forty mortar prisms of 10×10×5 mm for each type of binder were prepared. The dosage of mortars was prepared as follows:

MT1 mortar, prepared with hydraulic lime: binder/sand ratio = 1/1 and water/binder ratio = 0.6.

MT2 mortar, prepared with lime and pozzolana: lime:pozzolana:sand ratio = 1:1:6 and water/lime + pozzolana ratio = 0.8.

MT3 mortar, elaborated with ordinary Portland cement and MT4 mortar, prepared with mineralized white Portland cement. Mortars contained 20% (wt) of $CaCO_3$, with respect to the cement weight. Binder/sand ratio = 1/3 and water/binder ratio = 0.5.

Different curing procedures were followed as a function of the binder nature.

Hydraulic lime mortars (MT1): the moulds were maintained at 21 ± 1 °C and 98% RH for 1 day. Then the prisms were demoulded and kept at 21 ± 1 °C and 100% RH for 3 months. Then, prisms were carbonated until all portlandite was transformed into $CaCO_3$. Both, hydration and carbonation processes were followed by X-ray diffraction.

Lime–pozzolana mortars (MT2): the moulds were maintained at 50 °C and 100% RH for 3 days. The pieces were then demoulded and maintained at 50 °C and 100% RH for 4 days. Finally they were immersed in water at 50 °C for 3 extra days. After this, the specimens were dried in an oven at 50 °C for 3 h. They were let to cool and then moved to a carbonation chamber where they remained for about 36 days in a carbon dioxide environment at 21 °C and 50% RH. Prisms were carbonated until all portlandite was transformed into calcium carbonate. Carbonation process was followed by X-ray diffraction.

Ordinary Portland cement mortars (MT3) and white Portland cement mortars (MT4): the moulds were maintained at 21 ± 1 °C and 98% RH for 1 day. Then the prisms were demoulded and immersed in water for about 3 months (time until total reaction). Finally prisms were carbonated until all portlandite was transformed into $CaCO_3$. Reactions were followed by X-ray diffraction.

2.2. Exposure conditions

In order to perform exposure tests to simulate the possible formation of thaumasite, mortars underwent accelerated sulfation by exposing the samples to a 300 ppm SO_2 atmosphere at 25 °C and 95% RH for 2 days. Subsequently, one half of the sulfated samples were exposed for 6 and 12 months in chamber with 0.3 ppm. SO_2 as pollutant with $0.50\,\mathrm{l\,min^{-1}}$ flow gas velocity, 5 °C and 95% RH. The other halves of the sulfated samples were partially immersed in water at 5 °C for 4, 9 and 14 months. In order to ensure that the sulfation reactions would occur only on the exposed surface of the samples, a passivation treatment was applied to the samples by means of graphite paint on the five non-exposed faces of the prisms. It left an exposed surface of 1 cm^2 each sample.

2.3. Characterisation

After exposure for 6 and 12 months, the specimens were removed from the chambers, cleaned by removing the passivating graphite paint and preserved in an inert atmosphere. Samples partially immersed in water at 5 °C were respectively removed after 4, 9 and 14 months. The porosity together with the chemical and mineralogical and microstructural analyses were subsequently carried out by means of mercury intrusion porosimeter (MIP), ion chromatography (IC), infrared spectroscopy (FTIR) and electron microscopy (SEM–EDAX).

3. Results and discussion

3.1. Porosity

The total porosity of the specimens after exposure in chamber with 0.3 ppm of SO_2 for 6 and 12 months is shown in Table 1.

The test of simulation of polluted atmospheres to which were submitted our materials, do not produce substantial modifications in total porosity of the mortars. This characteristic (porosity), either remained similar after 12 months of exposure (sample MT4), or slightly increased (sample MT1, MT2 and MT3).

3.2. Soluble sulfate and sulfite

Sulfate and sulfite ions were measured by means of ion chromatography (IC) in samples submitted to intensive sulfation for 2 days. The data are reported in Table 2. The four mortars reacted intensely with the

Table 1
Total porosity of mortars

Exposure time	MT1 (cm^3/g)	MT2 (cm^3/g)	MT3 (cm^3/g)	MT4 (cm^3/g)
Non-exposed	0.142	0.134	0.069	0.066
6 months	0.128	0.117	0.076	0.074
12 months	0.154	0.145	0.074	0.067

Table 2
Ion chromatography (IC) analyses of sulfates and sulfites in mortars after accelerated sulfation by exposing the samples to 300 ppm SO_2, 25 °C and 95% RH for 2 days

Ions	MT1	MT2	MT3	MT4
$SO_3^=$ (mg/g)	3.817	3.182	1.891	1.565
$SO_4^=$ (mg/g)	5.972	7.48	7.974	7.871

polluting gas. In spite of the short period of time of this first exposure the amount of S incorporated by the samples was high, similar or even higher than the sulfur fixed by the cement and lime and pozzolana mortars after 90 days exposed into the environmental simulating chamber containing 3 ppm of SO_2 in the air [3].

The sulfite ion presence indicates that due to the action of the atmospheric SO_2, the sulfation process occurs through a mechanism of heterogeneous interaction with the following stages [4–6]: (a) SO_2 dissolution in water, giving place to the formation of sulfite ions and protons; (b) oxidation of the ion sulfite into ion sulfate. Therefore the ion sulfite is an intermediate product in the sulfation mechanism of the dry deposition of SO_2.

According to bibliography, the sulfation of the mortars mainly depends on the nature and on the porosity of the material. The higher the porosity, the greater the sulfation process. The relative reactivity of materials is as follows [3,7]:

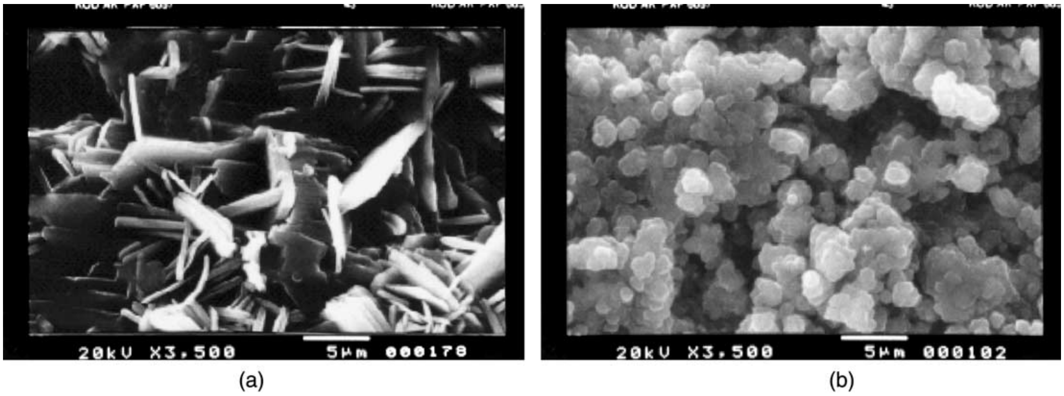
$$\text{Lime and pozzolana mortar} < \text{lime mortar} < \text{cement mortar}$$

Both MT1 and MT2 mortars, with the highest porosity, are also those resulting with highest sulfation; higher than that of cement mortars MT3 and MT4. In this last case the nature of the binder has less influence since during the carbonation process the portlandite of the cement mortars is replaced by calcite. Furthermore the mineralogical composition and the pH of the porous solution for cement mortars are (after carbonation), similar to those of the hydraulic lime or lime and pozzolana mortars. So, the amount of S fixed in the samples studied in these conditions is lesser dependent on the type of binder used than on factors like porosity and specific surface. In turn the sulfation process differs for both types of mortars since those made of cement fix the sulfur mainly in form of sulfates, whereas, mortars MT1 and MT2 fix it fundamentally as sulfite. That means that the oxidation process takes place for the cement mortars faster than for the other studied mortars [8].

3.2.1. *MT1—hydraulic lime mortars*

FTIR spectrum of the sample before being submitted to sulfation in chamber shows absorptions that are attributed to quartz, calcium carbonate and C–S–H gel. It is notable that the bands corresponding to the characteristic vibrations of SO_4 group are absent in sample. Spectra of samples exposed to SO_2 ambient in chamber disclosed a progressive fixation of S, so that vibration bands of the SO_4^{2-} group appear (600–700 cm^{-1} and 1100–1200 cm^{-1}). The frequencies at which these bands appear coincide with those of gypsum: ν_4 (603 and 669 cm^{-1}) and ν_3 (1120 and 1144 cm^{-1}). In these spectra, a decrease of the intensity of calcite bands can be observed in those samples exposed until 6 months. Spectrum of sample exposed for 12 months shows a new increase in the intensity of the bands of carbonate, while gypsum bands are not seen.

SEM/EDAX analyses allowed examination of the surface of the sample before being exposed and revealed different morphologies of C–S–H gel, with variable chemical composition. Moreover, in agreement with FTIR results, the presence of calcite crystals can be seen on the surface. SEM/EDAX analyses of the surface of the sample reflect clear signs of attack after 2 days of intensive sulfation. This is more evident after 6 months of treatment. The main product generated by this attack was gypsum. A large amount of gypsum crystals can be observed on the surface of the sample as shown in Fig. 1a. The gypsum amount increases with exposure time until 6 months. At the same time calcite fades away



(a) (b)

Fig. 1. SEM micrographs. MT1 sample. (a) 6 months exposed: gypsum layer formed on the sample surface, (b) sample 12 months exposed: poorly crystallised calcite crystals on the surface.

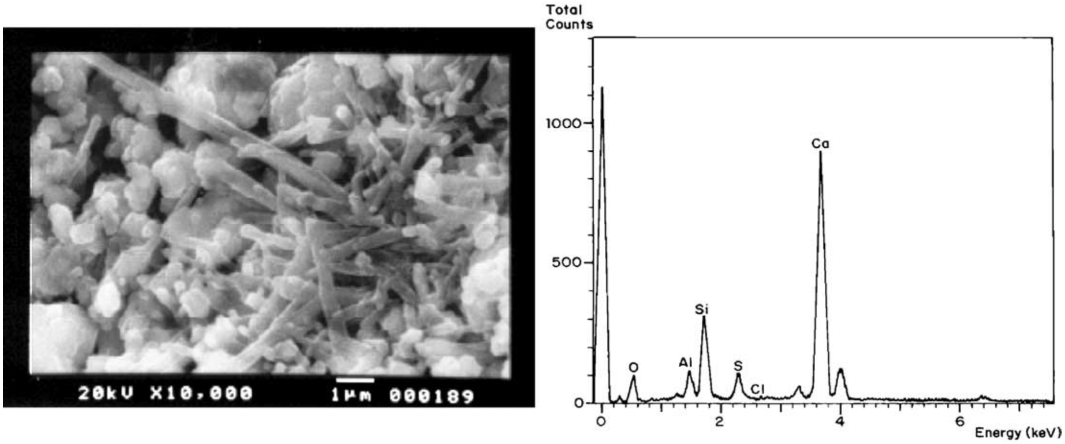


Fig. 2. MT1 sample. 4 months maintained at 5 °C, micrograph and EDAX analysis of needles identified as thaumasite or thaumasite–ettringite solid solution.

gradually. After 12 months of exposure, an important microstructural change was produced on the surface of the specimen: while gypsum crystals were not seen,poorly crystallised calcium carbonate crystals were observed on the surface of the sample (Fig. 1b).

The surface of the sample, which was partially maintained immersed in water for 4 months at a temperature of 5 °C, presented some gypsum crystals and some other needle shaped crystals, which might be identified as ettringite or thaumasite or even like a solid solution of both phases (Fig. 2). This sample immersed in water for 9 months at 5 °C, did not either present gypsum crystals, or calcite. The previously described needles were not seen at 9 months, however they were again observed on the sample surface after 14 months of curing.

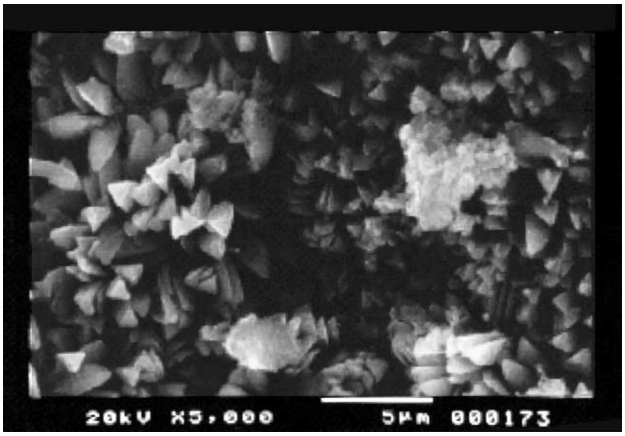


Fig. 3. MT2 sample before sulfation: calcite crystals on the surface.

3.2.2. MT2—lime and pozzolana mortars

Through FTIR, bands belonging to quartz, calcite and C–S–H gel were detected in samples before SO_2 exposure. Bands of the SO_4^{2-} group were absent. The analysis through FTIR, reveals the presence of S in specimens exposed for 2 days and 6 months to the SO_2 environment. Some bands due to SO_4^{2-} vibration appear in the spectra. Considering the frequencies at which these bands appear, ν_4 (602, 643, 657 cm^{-1}), ν_1 (979, 1000 cm^{-1}) and ν_3 (1104, 1139 and 1191 cm^{-1}), they could be regarded as syngenite. Additionally, because of the SO_2 effect, a decrease of the intensity of the calcite bands is observed. This clearly visible decrease in calcite from 2 days to 6 months of exposure is due to the transformation of calcite by SO_2 attack.

SEM–EDAX technique reveals the existence of different morphologies of the C–S–H gel in the specimen surface before sulfation, having variable chemical composition and containing some Al (Fig. 3). Additionally, the presence of calcite crystals on the surface becomes visible and confirms FTIR results. A change in the morphology of the specimen surface was observed after exposure experiments. Distinct signs of attack become stronger as treatment ran from 2 days to 6 months. The different analyses carried out show the progressive deposition of SO_2 (higher at 6 months), as well as the high amounts of the potassium, possibly coming from the leucite present in the employed pozzolana. Sulfur dioxide gives rise to the formation of syngenite $CaK_2(SO_4)_2$-H_2O, since crystals appear through the whole surface; analyses and morphology are in accordance with it (Fig. 4a) confirming the FTIR results. After 12 months of exposure in the simulation chamber, an important microstructural change is again produced on the surface of the specimen; syngenite crystals are not seen (Fig. 4b).

The MT2 sample maintained partially immersed in water for 4 months at 5 °C showed syngenite and gypsum crystals on the surface. The MT2 sample stored for 9 months in the same conditions did not contain syngenite; however, some gypsum and calcite could be identified on the surface. Small needles which could not be determined were newly seen, after 14 months of conservation in water.

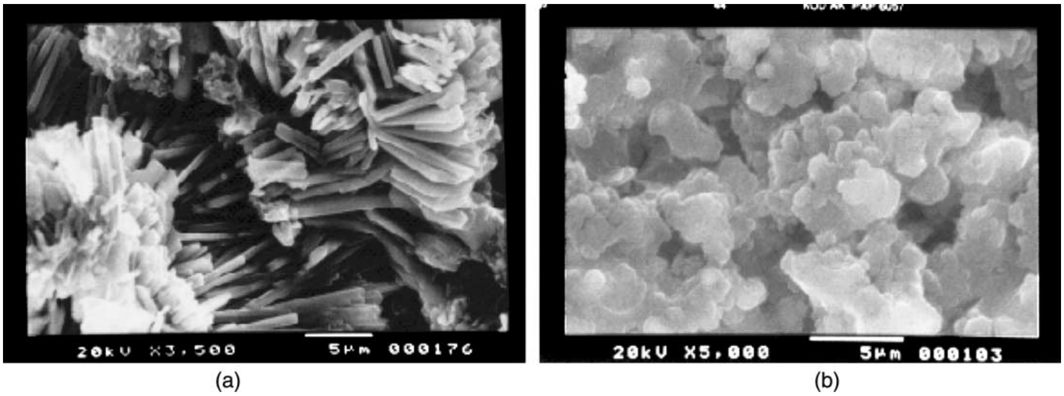


Fig. 4. MT2 sample. (a) 6 months exposed: syngenite crystals in the surface of the sample, (b) 12 months exposed: SEM micrograph of the surface.

3.2.3. MT3—low Al_2O_3 ordinary portland cement mortars

Through FTIR, the characteristic bands of carbonate group due to calcite, and Si–O vibration bands from the C–S–H gel and quartz are seen in samples before exposure tests. Results from FTIR analyses showed that two simultaneous processes had altered mortars after exposure tests: progressive fixation/stabilisation of sulfur, and decomposition of calcite. In the spectra, new SO_4 bands, which were due to the stabilisation of sulfur, appear in specimens with 2 days exposure. The intensity of those bands increased with time of exposure. It can also be seen a decrease of the intensity of the bands due to calcite, caused by decomposition due to SO_2 attack.

The study of the surface of the sample with SEM/EDAX before exposure tests, reveals the existence of different morphologies of C–S–H gels, with variable chemical compositions and ratio $C/S > 2$. In the whole specimen abundant calcite crystals appear as a result of a carbonation process of the superficial $Ca(OH)_2$. After exposure tests the increase of sulfur through the whole specimen, (C–S–H gel and aggregates) (Fig. 5) and the progressive elimination of the calcite on the surface of the sample were observed. At 6 months, no calcite is observed. After 12 months, layers of poorly crystallised calcium sulfate (probably gypsum), can be observed on the sample surface.

The sample maintained partially immersed in water for 4 months at a temperature of 5 °C, had some calcite crystals and C–S–H gel on the surface. Additionally, gypsum crystals together with some needles, which could be thaumasite, can be observed on the surface of the sample (Fig. 6). After 9 and 14 months, a lot of thaumasite crystals were seen on the MT3 surface (Fig. 7).

3.2.4. MT4—mineralized white portland cement mortars

FTIR spectra show the characteristic absorption bands due to calcite, quartz and C–S–H gel in samples without treatment in chamber. New bands due to SO_4^{2-} from sulfur fixation appear in specimens with 2 days exposure. The intensity of those bands increases with time of exposure. A decrease of intensity of the CO_3 bands from calcite is also observed.

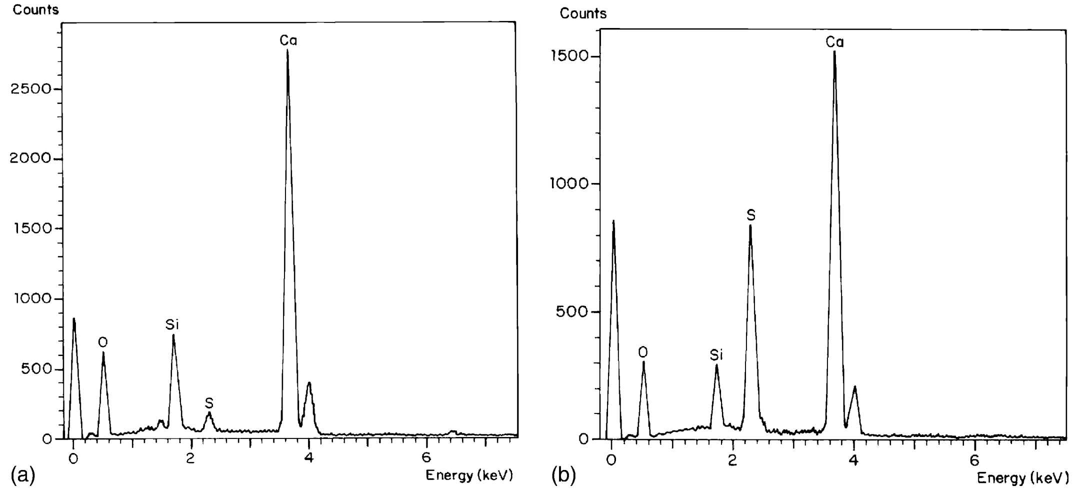


Fig. 5. MT3 mortars: (a) EDAX pattern of CSH gel of the sample after 2 days of intensive sulfation, (b) after 6 months of exposure in the simulation chamber.

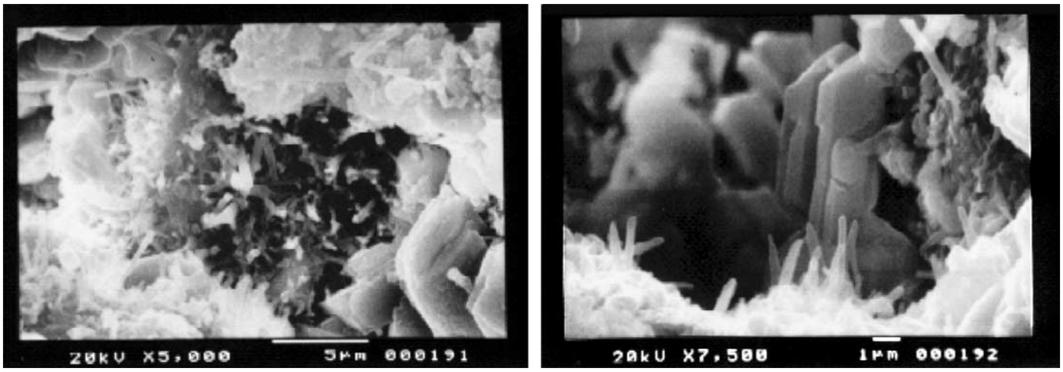


Fig. 6. SEM micrographs. MT3 sample after 4 months partially immerse in water. Small crystals of thaumasite.

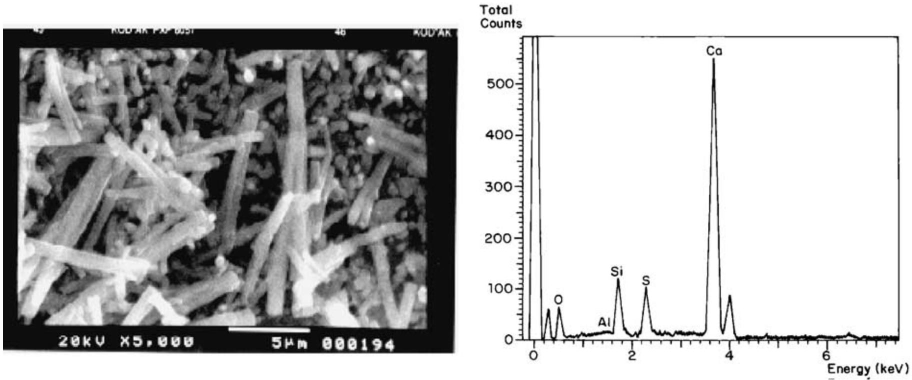


Fig. 7. MT3 sample after 4 months partially immerse in water. SEM microphotography of well developed crystals of thaumasite and EDAX pattern.

By studying the surface of the sample without treatment in chamber, by SEM/EDAX, different morphologies of C–S–H gel, together with abundant calcite crystals from superficial carbonation have been observed. Sulfur appears on the different morphologies of the C–S–H gel, with a remarkable increase at 6 months of exposure. Moreover, the attack could cause the decomposition of calcite crystals on the surface since the amount of this compound diminished after 2 days of intensive sulfation. After 6 and 12 months of exposure, many gypsum and no calcite crystals can be seen.

Additionally, after 6 months of exposure, a group of needles (maximum 10 μm length and 0.25 μm thick) appears on the specimen. The shape and composition (Fig. 8) suggest that it could be a mixture of gypsum, ettringite and /or thaumasite, but the identification was not conclusive.

Finally, the surface of the sample maintained partially immersed in water for 4 months at temperature of 5 °C, showed some calcite crystals and a C–S–H gel very rich in sulfur. Some gypsum crystals and some needles, which could be thaumasite, can be observed on the

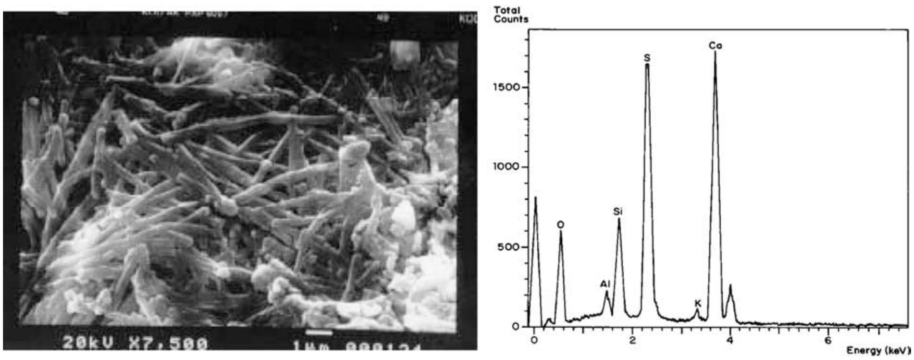


Fig. 8. MT4 sample. 6 months in chamber. SEM microphotography and EDX of the needle shaped crystals; likely thaumasite–ettringite and gypsum.

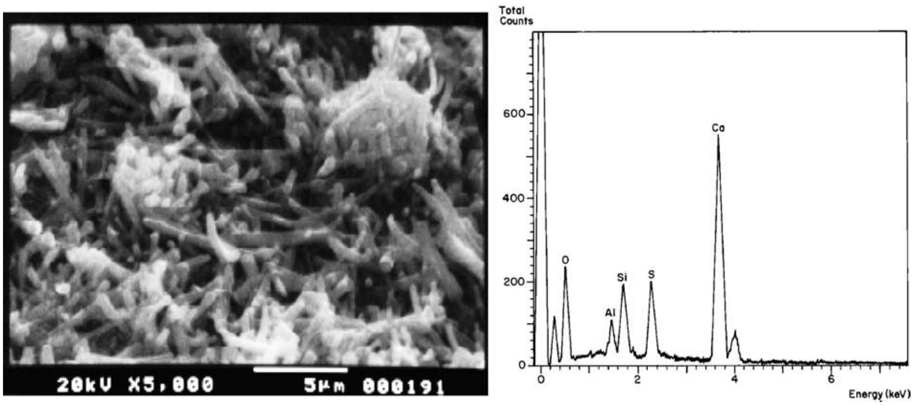


Fig. 9. MT4 after 4 months in water. Microphotography and EDX of thaumasite crystals or thaumasite–ettringite solid solution crystals.

surface of the sample, too (Fig. 9). After 9 and 14 months of storage in water, the size of needles have increased and thaumasite clearly remains in the samples.

Therefore the simulation test in climatic chamber, with a continuous flow of SO_2, carried out on hydraulic mortars trying to reproduce the environmental thaumasite formation have not reached such an objective; only in the sample MT4 were some crystals with acicular shape were identified. Those crystals could be a mixture of gypsum, ettringite and/or thaumasite. However, the process of thaumasite formation has been reproduced in the mortars prepared with hydraulic lime or with Portland cements (without or with low calcium aluminate contents) submitted to the following processes: (a) carbonation, (b) accelerated sulfation and (c) immersion in water at 1–5 °C, during several months. Under these same conditions thaumasite is not detected in lime and pozzolana mortars, neither at 4 months of test nor at 9 months.

The main differences between the two types of tests arise from the storage conditions: on one hand, the submerged samples absorbed a lot of water that would facilitate the dissolution and transport of ions and consequently the thaumasite formation; on the other hand, in the chamber test, the samples were exposed to the a continuous SO_2 action, increasing their sulfates content (which could favoured the thaumasite formation) but generating a continuous acidity in the medium, what could prevent the formation of thaumasite. Additionally, mortars were exposed for a long period of time to CO_2 action which could decompose the thaumasite formed. These results agree with some other data described in Ref. [9] where thaumasite was found in the internal part of the mortars where there existed a high humidity level and low concentrations of CO_2.

4. Conclusions

1. Thaumasite formation in hydraulic mortars owing to the interaction of the material with SO_2, has been reproduced in the hydraulic lime and cement mortar samples. Thaumasite was not formed in the lime pozzolana mortars (MT2).
2. Cement mortars have higher tendency to form thaumasite than hydraulic lime.
3. Gypsum is the first product formed as a result of the interaction hydraulic mortar–SO_2. Subsequently, gypsum reacts with calcium carbonate and C–S–H gel giving place to thaumasite.
4. The simulation tests carried out into the weathering chambers (continuous flow of SO_2 on hydraulic mortars) have not achieved the objective of reproducing the thaumasite formation. Gypsum is initially formed but no thaumasite; only in sample MT4 exposed for 12 months, were some needle shaped crystals (they could be a mixture of gypsum, ettringite and/or thaumasite) identified.
5. The formation of thaumasite was easier and quicker in sulfated samples stored at low temperature and partially immersed in water.

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