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The effect of temperature on thaumasite formation

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ABSTRACT

In this study mortars have been produced using ordinary Portland cement (CEM I – 32.5) and limestone cement with 15% limestone addition (CEM II/A-LL – 32.5). The mortars were immersed in a solution of 5% Na_2SO_4 at 5 °C, 10 °C and 20 °C for 1 year and the caused deterioration was visually observed on a regular basis. The deterioration product on the surface of the mortars has been identified as thaumasite by means of XRD, FT-IR, DTG and SEM/EDAX analyses. Mortars immersed in a solution of 5% Na_2SO_4 at 10 °C for a year suffered limited surface damage, which was identified as thaumasite formation and carbonation. Similar damage appeared for mortars immersed in a solution of 5% Na_2SO_4 at 5 °C for 6 months and that led to the conclusion that thaumasite formation is related inversely to the conservation temperature of the mortars. Finally, mortars immersed in a solution of 5% Na_2SO_4 at 20 °C for a year were intact and thaumasite could not be identified.

1. Introduction

Thaumasite $[Ca_3Si\,(CO_3)(SO_4)(OH)_6 \cdot 12(H_2O)]$ is a rare naturally occurring mineral that has been known for at least the last 100 years and it can also be synthesized in the laboratory [1]. During the last few years it has been apparent that thaumasite can be formed in cementitious materials in the field and in the laboratory, destroying the connectivity of the cement paste [2–4].

The literature on thaumasite synthesis describes the conditions under which the synthesis is accomplished:

(i) Temperature: a range of 0–5 °C is preferred for the following reasons:
   - Kleber's rule: a decrease of the temperature leads to an increase in the coordination number and vice versa. Thus, a low temperature lets the Si coordination sphere expand enough to form $[Si(OH)_6]^{2-}$; and
   - low temperatures favour the solubility of the calcium salts necessary for the synthesis.

(ii) Humidity: a high humidity level promotes the transport of the ions needed for the synthesis: SO_4^{2-} and CO_3^{2-}.
(iii) Time: thaumasite synthesis is a long process that involves the expansion of the Si coordination sphere [1].

In general, the standards that regulate the use of Portland cement in sulphate aggressive environments limit the content of aluminates in cements, in order to avoid formation of expansive ettringite. In other words, standards consider ettringite formation as the only sulphate related risk for the durability of hydrated Portland cement. It is noteworthy that no prevention is considered regarding the destructive action on concrete from possible thaumasite formation, one of the reasons being the difficulty of detecting this compound in deteriorated concrete [5–7].

Expansive ettringite formation in hydraulic concrete (due to sulphate attack) can be prevented, avoiding thereby its destructive effect. In case of thaumasite this is not yet possible, since the mechanism of thaumasite formation is not well known [8,9].

According to different researchers of this subject, thaumasite formation can be the result of different mechanisms: it can be the consequence of the ettringite evolution, incorporating Si^{4+} in its structure, substituting Al^{3+} ions within the columns $Ca_6[Al(OH)_6]^2$ and the interstitial replacement of $(SO_4)_3 \cdot 2H_2O$ by $(SO_4)_2 \cdot (CO_3)_2$ [10–14], or it can be the result of the interaction of sulphates and carbonates that can be present in the aqueous phase of the concrete, with C–S–H gel [13–16].

$$3Ca^{2+} + SiO_3^{2-} + CO_3^{2-} + SO_4^{2-} + 12H_2O \rightarrow 3CaO(SiO_2)(CO_3)(SO_4) \cdot 12H_2O$$

Both mechanisms might develop simultaneously within the same material but the fact is that thaumasite consists of three different anions: carbonate, sulphate and silicate in the form of $Si(OH)_6$ associated with calcium cations. A source of all these ions is therefore required for thaumasite to form. In cements, the silicate ions are derived from the bulk phase within the cement paste,

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which is the main reason why the cement loses its integrity during thaumasite sulphate attack (TSA). The source of the sulphate ion is generally considered to be external, normally derived from the groundwater. In a mortar or concrete containing either carbonate aggregates or limestone filler as part of the cement, the carbonate ion will be derived predominantly from these sources. However, these cannot be the only source because thaumasite sulphate attack (TSA) has been found in siliceous aggregate mortars and concretes made with cement containing no limestone addition [16]. It seems that either the aggregate or binder is contaminated or the source of carbonate ions must be external and are present due to atmospheric carbonation [17].

In field cases it has been reported that thaumasite is formed in temperatures that range between 0 °C and 25 °C [16,18–22].

The aim of this study is to investigate how thaumasite formation evolves in different temperatures (5 °C, 10 °C, and 20 °C) as well as different mortars with or without limestone addition. The formation of thaumasite is confirmed using different analytical techniques, and the effect of thaumasite sulphate attack on the mechanical properties of the mortars is also monitored.

2. Experimental program

In this study, mortars have been produced using ordinary Portland cement (CEM I – 32.5) and limestone cement with 15% limestone addition (CEM II/A-LL – 32.5). Chemical analysis of these cements is presented in Table 1.

The mortars that were produced had w/c ratio 0.5 and siliceous sand according to the EN-196-1. The specimens were of size 4 × 4 × 16 cm, and were preserved for two days in the mould inside a wet chamber, another 12 days inside a saturated solution of calcium hydroxide at 20 °C in order to gain strength, and finally for 6 months inside a 5% Na_2SO_4 solution at 5 °C, 10 °C and 20 °C while the pH of the solution was highly alkaline around 14. [23,24] The above method aimed at accelerating the deterioration process.

The specimens were visually inspected on a regular basis in order to appreciate the damage. Compressive strength was also measured, at 28, 56, 90, 180 and 365 days, to detect the influence of microstructural changes on the mechanical properties of the mortars. Finally, expansion of the specimens was measured on a weekly basis using an appropriate micrometer in order to determine whether microstructural changes combined with expansion.

After 1 year samples from the damaged surface of the mortars were taken to identify the nature of the product. Identification was made using X-ray diffraction (XRD), infrared spectroscopy (FT-IR), differential thermogravimetric analysis (DTG), scanning electron microscope (SEM) and X-ray microanalysis (EDAX).

Table 1
Chemical analysis of cements

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
0% LL	20.05	4.40	3.17	65.25	3.12	0.64	0.14	3.29	2.6
15% LL	17.82	3.86	2.88	69.30	2.82	0.59	0.13	3.00	8.28

3. Results and discussion

3.1. Visual inspection

The specimens were visually examined on a regular basis. Photographs of the 1-year mortars are shown in Fig. 1. After 1 year of immersion in a solution of 5% Na_2SO_4 at 5 °C all four surfaces of the specimens turned into a white cover that was friable and started to peel off leaving the aggregates uncovered and reducing the connectivity of the paste. Specimens that have been immersed in a solution of 5% Na_2SO_4 at 10 °C for a year presented the above-mentioned damage in only one of the four surfaces, which was the surface that did not come in contact with the mould during the construction process. This likely happened because this surface has a larger porosity and the ions could penetrate more easily. It is noteworthy that the specimens that were preserved at 10 °C had approximately the same damage that specimens preserved in a solution of 5% Na_2SO_4 at 5 °C had at the age of 6 months, which was also limited only in one surface of the mortars [25]. The specimens preserved in a solution of 5% Na_2SO_4 at 20 °C for a year did not present any surface damage. Both mortars, with and without limestone addition, had the same behaviour under the same preservation conditions and it seems that the damage proceeds independently of limestone addition. Consequently, the specimens' surface damage appears to be inversely related to the temperature of conservation.

The mortars were sectioned so that not only the surface but all the mass of the mortar could be examined macroscopically and the extent of the damage could be measured. This test showed that the damage, if present, was limited to the surface layer for all mortars and all temperatures.

3.2. Identification of the deterioration products

In order to positively identify the deterioration products and be certain of the result different analytical methods were used. The main problem related to identification is that thaumasite and ettringite have structural similarity. Only the joint results of several analytical methods as follows can lead to a reliable conclusion about the formation of thaumasite.

3.2.1. X-ray diffraction

In order to determine the nature of the deterioration products the damaged area was examined using X-ray diffraction (XRD) analysis. XRD patterns of deteriorated parts of the mortars are shown in Figs. 2 and 3. The two patterns of the mortars preserved at 5 °C are quite similar, and the main peaks that have been recognised are those of thaumasite, calcite and quartz. Positive identification of thaumasite was made based on the peaks at 2θ 9.2°, 16.04°, 18.5°, 19.3°, 23.5° and 28.0°. The strongest peaks are at 2θ 9.2° with relative intensity 100%, at 2θ 16.04° with relative intensity 29% and at 2θ 23.5° with relative intensity 37%. Absence of peaks at 2θ 15.8°, 18.9°, 22.9° and 26.5° indicates that no ettringite is present in the deterioration product. [26] It is noticeable that in spite of the fact that no calcite was added in the synthesis of the mortar without limestone the deterioration product has peaks

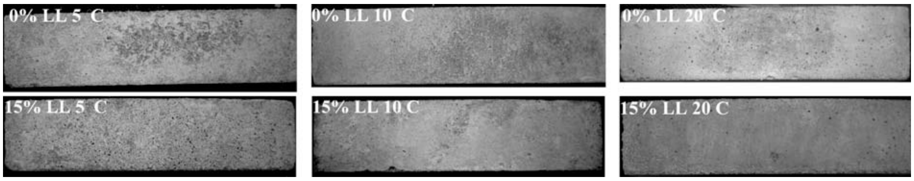

Fig. 1. Macroscopic images of mortars preserved at a solution of 5% Na_2SO_4 for a year.

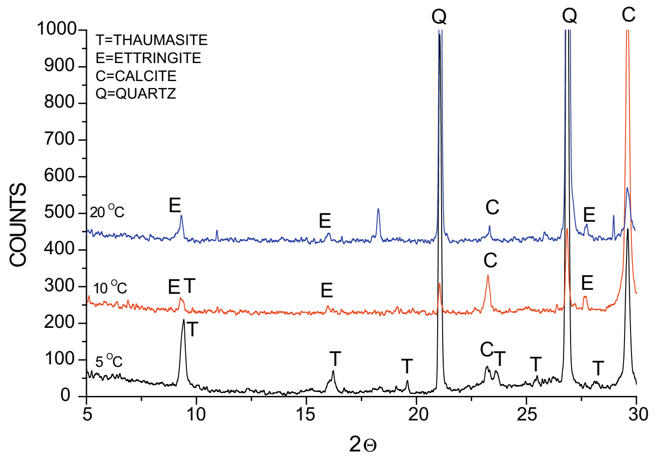

Fig. 2. XRD patterns of the damaged surface of the mortars with 0% limestone.

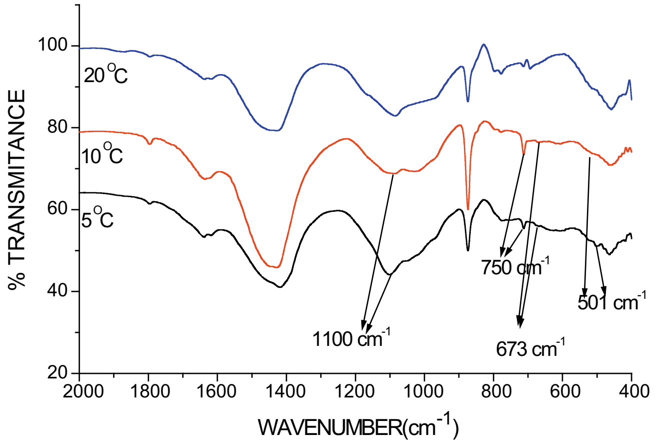

Fig. 4. FT-IR spectra of the damaged surfaces of the mortars with 0% limestone.

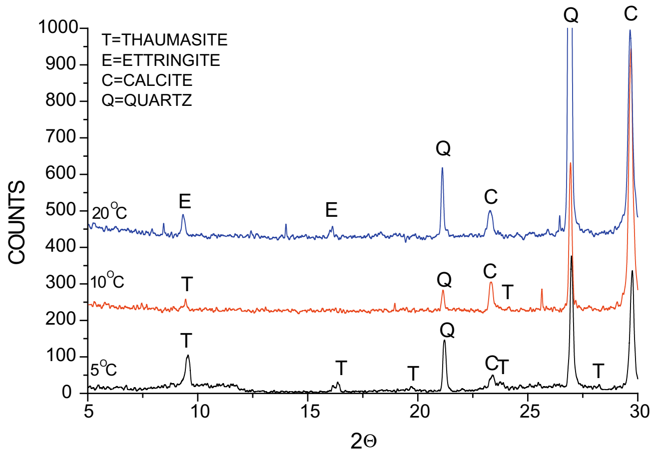

Fig. 3. XRD patterns of the damaged surface of the mortars with 15% limestone.

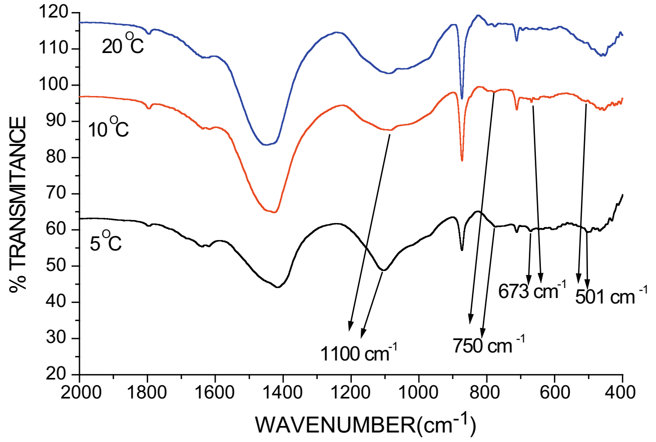

Fig. 5. FT-IR spectra of the damaged surfaces of the mortars with 15% limestone.

attributed to calcite such as that at 2θ 23.0° and 29.9° 2θ. Furthermore there is a complete absence of hydration products of cement such as portlandite in either mortar. The two patterns of the mortars preserved at 10 °C are also similar and indicate the existence of thaumasite that coexists with ettringite, especially in the mortar without limestone addition because it has a higher amount of C_3A. The main observation in these patterns is that the calcite peaks are considerably high in both mortars, which indicates high carbonation of the mortars. This is also an observation that was made in the mortars preserved at 5 °C for 6 months and it seems that the specimens preserved at 10 °C follow exactly the same pattern of deterioration of the mortars preserved at 5 °C, but with a 6 months time hysteresis. The results of the analysis of the specimens preserved at 5 °C for 6 months are presented in Pipilikaki et al. [25]. Lastly, the patterns of the specimens preserved at 20 °C had the main peaks of ettringite, calcite and quartz, and do not indicate existence of thaumasite.

3.2.2. Infrared spectroscopy (FT-IR)

The XRD analysis is indicative of the nature of the deterioration products but further investigation is needed to confirm the results. This investigation was made using FT-IR spectroscopy and the FT-IR spectra of the damaged surface are shown in Figs. 4 and 5. The starting point for identification and characterization of thaumasite through FT-IR spectroscopy is the absorption bands of the structural groups of the compound. Consequently, the presence of thaumasite has to be verified in the corresponding spectrum by its characteristic bands of the groups SiO_6, CO_3, SO_4 and OH. This method is appropriate for the study of thaumasite formation, because it allows identification of a phase in which silicon is octahedrally coordinated. Octahedral silicon is very rare in cement mortars, and is attributed to thaumasite. Bands due to SiO_6 group vibrations appear near 500, 555, 673, 750, and 1075 cm^{-1}. At 871 cm^{-1}, thaumasite has a wide and weak band due to CO_3 vibration, this band is interfered with the one corresponding to calcite when this compound appears together with thaumasite, which happens quite frequently. At 1065 cm^{-1}, the band is considered characteristic of the SiO_6 group vibrations, while at 1100 cm^{-1} SO_4, intensely overlaps it [26].

The spectres of the mortars preserved at 5 °C and 10 °C have all the above-mentioned bands, which clearly prove the existence of thaumasite in the deteriorated surface of the mortars. The peak at around 500 cm^{-1}, attributed to the SiO_6 group, proves the existence of thaumasite in these mortars. It is also noticeable that the specimens preserved at 10 °C present a large peak at 871 cm^{-1}, which is attributed to calcite and supports the result obtained by XRD analysis about the existence of an amount of calcite in these mortars. In the spectra of the mortars preserved at 20 °C, no peak is observed at 500 cm^{-1}, indicating absence of thaumasite.

3.2.3. Differential thermogravimetric analysis (DTG)

Differential thermogravimetric analysis (DTG) curves of the damaged surfaces of the mortars are presented in Figs. 6 and 7.

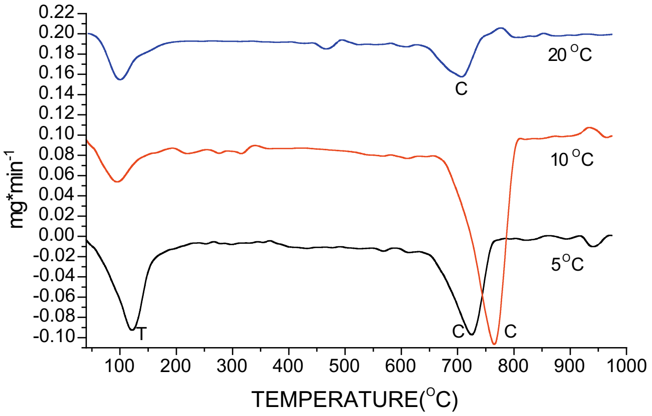

Fig. 6. DTG curves of the damaged surfaces of the mortars with 0% limestone.

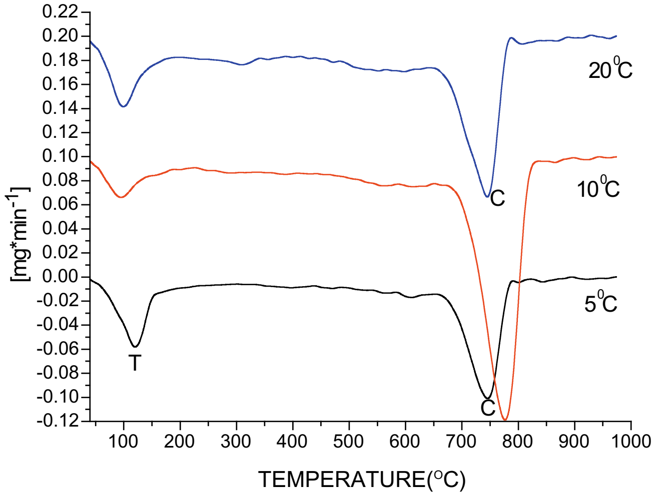

Fig. 7. DTG curves of the damaged surfaces of the mortars with 15% limestone.

The peak at around 130 °C is attributed to the dehydration of thaumasite, which is an irreversible process. The peak at around 700 °C is attributed to the loss of CO_2 and is connected to the existence of calcite. The fact that there is a strong peak at that temperature in the DTG curve of the mortar with no limestone addition supports the result that the mortar has suffered carbonation. Furthermore, the DTG curves show absence of products of hydration of cement such as portlandite in the curves of the mortars preserved at 5 °C and 10 °C. This supports the idea that portlandite has turned to calcite through carbonation.

3.2.4. Scanning electron microscope (SEM)

To complete the investigation of thaumasite formation a study using Scanning electron microscope (SEM) and X-ray microanalysis was necessary. Characteristic images of the damaged surfaces of the mortars preserved at 5 °C, 10 °C and 20 °C are shown in Figs. 8–10, respectively. In Fig. 11 a characteristic image of the intact inside of the mortars with and without limestone addition at 5 °C is presented.

In Figs. 8 and 9 the morphology shows hexagonal prismatic needle-shaped crystals in both photographs, attributed to thaumasite. [27,28] In the images some parts of C–S–H are also present. X-ray microanalysis of the crystals, presented in Table 2, shows that they have the chemical composition of thaumasite with calcium, silicon and sulphur being present while there is no aluminium peak that would indicate presence of ettringite. This last result proves without any doubt the formation of thaumasite in the surface of the mortars immersed in a solution of Na_2SO_4 at 5 °C and 10 °C for a year.

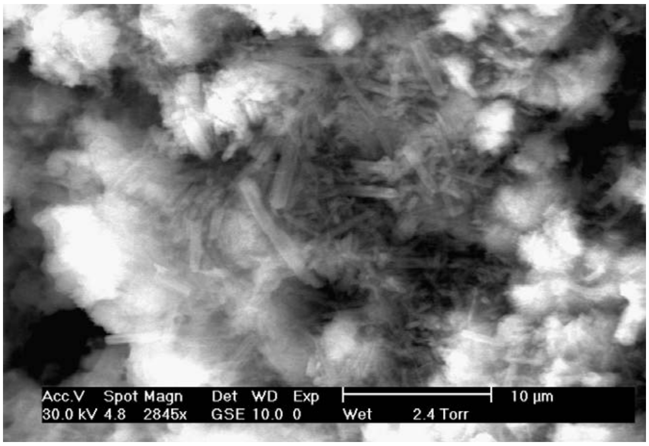

Fig. 8. Characteristic SEM images of the damaged surface of the mortars after 1 year of immersion in a solution of 5% Na_2SO_4 at 5 °C.

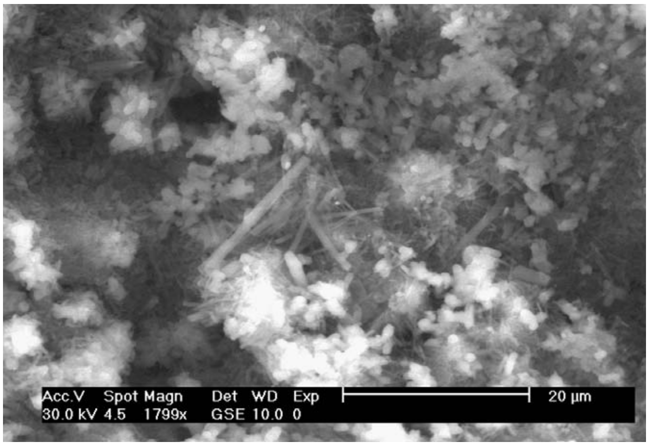

Fig. 9. Characteristic SEM images of the damaged surface of the mortars after 1 year of immersion in a solution of 5% Na_2SO_4 at 10 °C.

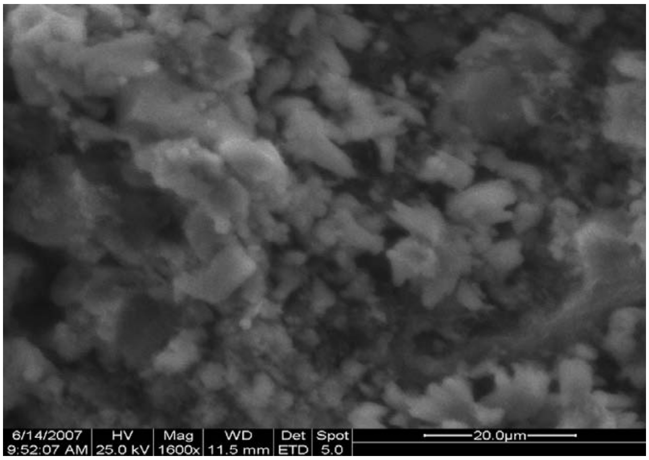

Fig. 10. Characteristic SEM images of the damaged surface of the mortars after 1 year of immersion in a solution of 5% Na_2SO_4 at 20 °C.

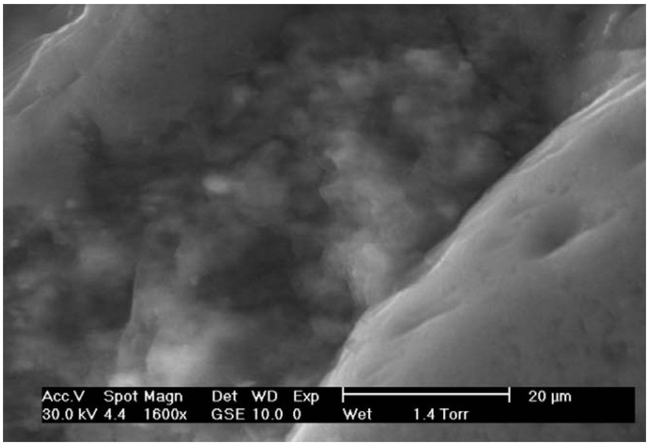

Fig. 11. Characteristic SEM images of the intact inside part of the mortars after 1 year of immersion in a solution of 5% Na_2SO_4.

Table 2
Results of EDAX analysis of the crystals of thaumasite observed in the mortars surfaces

	Theoretical value	Measured by EDAX analysis value
SiO/CaO	0.36	0.3
SO_3/CaO	0.4	0.3

As far as the mortars preserved in 20 °C (Fig. 10) as well as the inside of all mortars (Fig. 11) are concerned, the morphology is normal and does not present any alterations that could be considered as thaumasite formation.

3.3. Compressive strength and expansion

In order to determine the effect of conservation temperature on compressive strength and expansion and how these properties connect, expansion and compressive strength of the mortars were measured versus time of immersion in a solution of Na_2SO_4, and the results are presented in Fig. 12. In these diagrams the combined effect of both low temperature and the presence of sulphates solution are demonstrated resulting in the decrease of both mortars compressive strength.

As far as expansion is concerned, it does not follow the above-mentioned pattern and it is greater in the case of the mortars immersed in a solution of Na_2SO_4 at 20 °C. This indicates that thaumasite formation as far as this study is concerned is not related to expansion.

4. Conclusions

From the visual observations it is clear that both mortars immersed in a solution of Na_2SO_4 at 5 °C for 1 year, with and without 15% limestone addition, have severe surface damage. More specifically, the surface has started to peel off leaving the aggregates uncovered. Identification of the deterioration products of the mortars by means of XRD, FT-IR, DTG, SEM and EDAX has clearly shown the existence of thaumasite in the surface. It is also clear that no hydration products of cement exist in the outer zone, which explains why the paste is friable.

From the visual observations it is clear that both mortars immersed in a solution of Na_2SO_4 at 10 °C for a year, with and without 15% limestone addition, present some damage on only one surface, and they look like the mortars immersed in a solution of Na_2SO_4 at 5 °C for 6 months. Identification of the deterioration products of

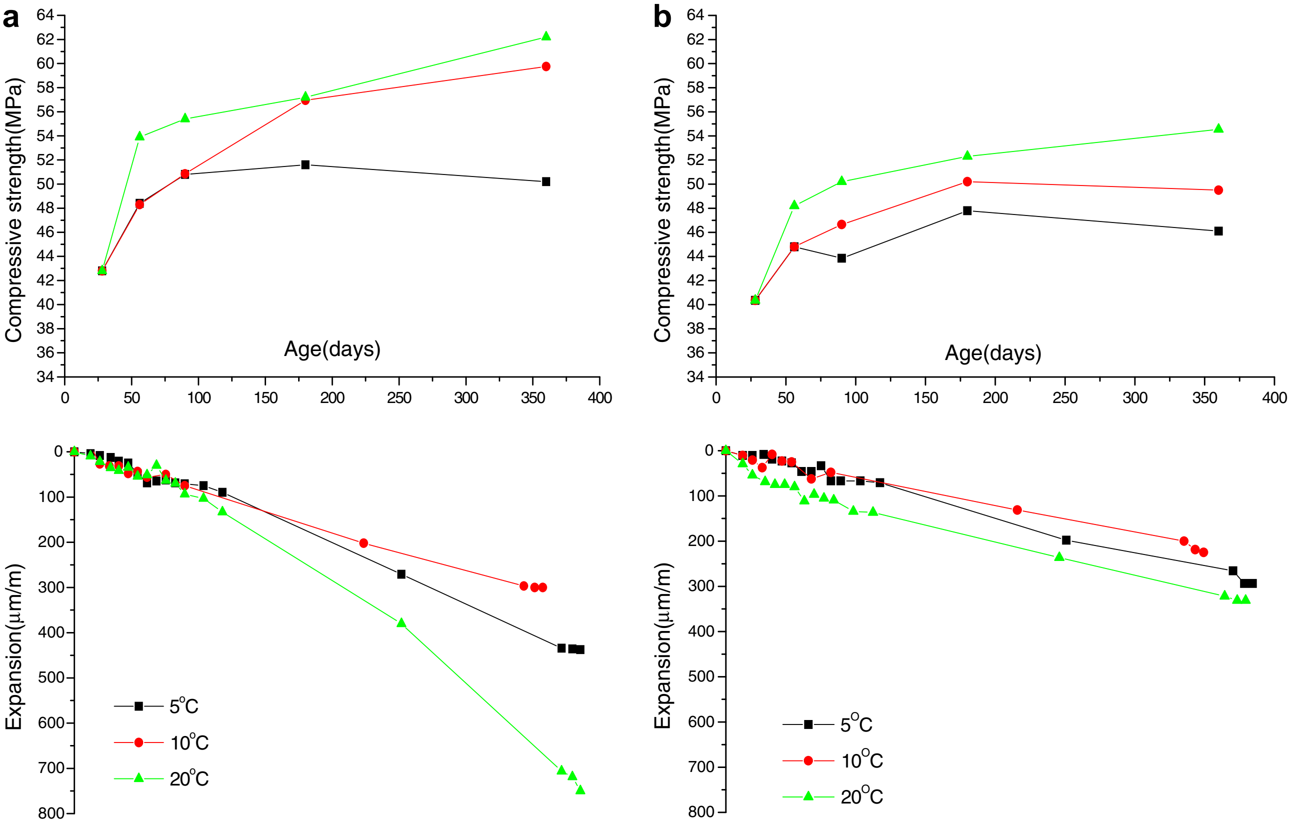

Fig. 12. Effect of temperature of conservation in a solution of 5% Na_2SO_4 on compressive strength and expansion of mortars: (a) with 0% limestone and (b) with 15% limestone.

the mortars has shown the existence of thaumasite in the surface but the most noteworthy observation is the existence of calcite, which is the predominant phenomenon of thaumasite formation. It is evident that thaumasite formation in a mortar is related inversely to temperature of conservation.

From the visual observations it is clear that both mortars immersed in a solution of Na_2SO_4 at 20 °C for a year, with and without 15% limestone addition, remain intact. For those specimens, none of the analytical techniques shows presence of thaumasite.

Limestone addition in cement mortars does not seem to have any detrimental effect on thaumasite formation in the range used in this study, because limestone cannot dissolve in such an environment. On the other hand carbonate and sulphate ions are necessary for thaumasite formation and it seems that both are from external sources. This is also the reason why thaumasite formation is limited only in the surface of the mortars.

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