



The effect of temperature on thaumasite formation

P. Pipilikaki^a, D. Papageorgiou^b, Ch. Teas^b, E. Chaniotakis^b, M. Katsioti^{a,*}

^a School of Chemical Engineering, National Technical University of Athens, 9 Heron Polytechniou Street, 15773 Zografou, Athens, Attica, Greece

^b Titan Cement Company S.A., Department of R&D and Quality, Elefsina, Greece

ARTICLE INFO

Article history:

Received 24 August 2007

Received in revised form 2 September 2008

Accepted 4 September 2008

Available online 13 September 2008

Keywords:

Thaumasite

Sulphate attack

Limestone cement

Sodium sulphate

Microstructure

Temperature

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% Na₂SO₄ 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% Na₂SO₄ 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% Na₂SO₄ 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% Na₂SO₄ at 20 °C for a year were intact and thaumasite could not be identified.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Thaumasite [Ca₃Si(CO₃)(SO₄)(OH)₆ · 12(H₂O)] 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:

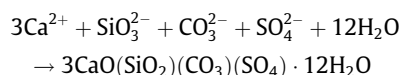
- (i) Temperature: a range of 0–5 °C is preferred for the following reasons:
 - Kleber's rule: a decrease of the temperature leads to an increase in the coordination number and vice versa. Thus, a low temperature lets the Si coordination sphere expand enough to form [Si(OH)₆]²⁻; and
 - low temperatures 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: SO₄²⁻ and CO₃²⁻.
- (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 Si⁴⁺ in its structure, substituting Al³⁺ ions within the columns Ca₆[Al(OH)₆]² and the interstitial replacement of (SO₄)₃ · 2H₂O by (SO₄)₂ · (CO₃)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].



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,

* Corresponding author. Tel.: +30 210 7723206; fax: +30 210 7723188.
E-mail address: katsioti@central.ntua.gr (M. Katsioti).

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% Na₂SO₄ 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 ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	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% Na₂SO₄ 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% Na₂SO₄ 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% Na₂SO₄ 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% Na₂SO₄ 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

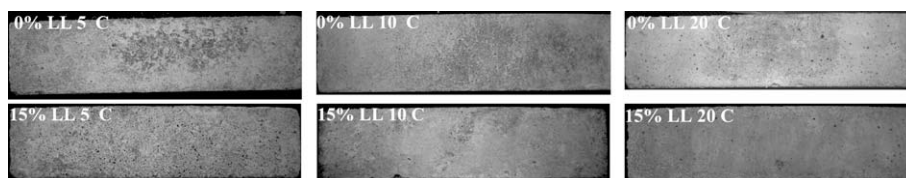


Fig. 1. Macroscopic images of mortars preserved in a solution of 5% Na₂SO₄ for a year.

Download English Version:

<https://daneshyari.com/en/article/1455465>

Download Persian Version:

<https://daneshyari.com/article/1455465>

[Daneshyari.com](https://daneshyari.com)