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# Ettringite dependance in thaumasite formation

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**Abstract.** Thaumasite has been synthesized with and without ettringite in the reaction medium. The compositions of solids have been analyzed over time by means of X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM-EDX) in order to check the relation between ettringite and thaumasite. The results indicate that in the synthesis in absence of ettringite, the thaumasite appears at 6 months. By contrast, in the synthesis with presence of ettringite, at 7 days much of the ettringite has become thaumasite and at 2 months ettringite has disappeared and only thaumasite is detected. The results obtained at the end of two years experience, using the Rietveld method, show that thaumasite forms from ettringite by substitution of aluminum with silicon.

## 1. Introduction

Thaumasite is a mineral formed by calcium carbonates, silicates and sulfates  $\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)(\text{CO}_3) \cdot 12\text{H}_2\text{O}$  and the interest in its study in cement based materials is relatively recent and topical [1-5]. Cases of roads and public highways where an abundant presence of thaumasite was detected in highly degraded concrete started to appear in the UK during the late 1990s [6], which led to the creation of a panel of experts from different institutions that were entrusted with the study of this issue [7]. The British interest materialized in the organization of a monographic conference in June 2002, [8] to which numerous case studies and research works were presented. The texts discussed during that conference shape an interesting themed volume with over 50 articles, which constitutes a very useful source of material when it comes to studying thaumasite [9].

Thaumasite is morphologically and structurally very similar to ettringite  $3\text{CaOAl}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$  [10, 11] which explains why interpretation mistakes have often been made, identifying as ettringite what could actually be thaumasite. These mistakes may occur after rapidly interpreting X-ray diffraction spectra, since the characteristic peaks of both minerals are very close to one another.

Whereas ettringite formation has been extensively studied and ettringite is widely believed to form through a reaction of sulfates with the hydrated calcium aluminates of cement, a certain degree of controversy still exists around the formation of thaumasite and its possible connection with ettringite. Nevertheless, the current state of knowledge can roughly be grouped together around the three following theories [12, 13]:

- 1) According to the first theory, thaumasite is formed through ettringite by substitution of aluminum for silicon.
- 2) In the second case, ettringite acts as a nucleator for the thaumasite formation.
- 3) According to the third theory, thaumasite could be formed directly without influence of ettringite in the process at all.



This paper aims to present an experiment designed to test the influence of ettringite in the formation of thaumasite. The experience is based on a synthesis of thaumasite in the absence and presence of ettringite (hereafter Th series and Ett series respectively).

Several studies have been conducted synthesizing thaumasite in the laboratory. While Aguilera *et al.* [14] carried out a direct synthesis using pure reagents in stoichiometric proportions; the study by Kohler, Heinz [15] utilizes synthetic cement clinker phases, fly ash and nanosilica as pastes in an aqueous solution, to which calcite and gypsum or sodium sulfate are added. Of these two possibilities, the synthesis proposed by Aguilera, Varela [14] was used as a reference and basis of our work, as it is easier to control because it uses pure reagents and seems to get a higher concentration of thaumasite.

The studies carried out by Barnett *et al.* [16-18] succeeded in drawing a distinction between ettringite and thaumasite by cell parameter refinement of the structure in these two minerals. In fact, they prefer to consider compounds as ettringite-type and thaumasite-type depending on the structural similarities with pure crystals, in the belief that a gap or discontinuity exists in the solid solution, that ettringite allows Si to replace up to 1/2 of its Al atoms, and that thaumasite can tolerate little or no replacement of Si with Al atoms.

## 2. Materials and methods

The thaumasite synthesis procedure suggested by Aguilera *et al.* [14] (*Th series*) consists of the following steps: (1) preparing a *solution A* of CaO in an aqueous solution; (2) preparing a *solution B* with the rest of the necessary components/elements, that is, Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>. A certain amount of sucrose is subsequently added to both solutions in order to avoid an excessive precipitation of by-products –unwanted secondary calcium compounds which would strongly reduce the performance of this reaction; and (3) these two solutions are mixed inside a polyethylene container hermetically closed before introducing it in the fridge at 5 °C. The concentrations of the different reagents in the mix are as follows: 0.025 M CaO, 0.006 M Na<sub>2</sub>SiO<sub>3</sub>, 0.006 M Na<sub>2</sub>CO<sub>3</sub> and 0.01 M Na<sub>2</sub>SO<sub>4</sub>. After some time, the samples are taken out of the fridge, filtered, dried and analyzed.

Instead, the modification through modified thaumasite synthesis (*Ett series*) consisted in adding previously synthesized ettringite to the medium through a process based on the method developed by Cody, Lee [19]. Two solutions, C and D, were prepared for this purpose: a *Solution C* with CaO in distilled water (0.185 gr CaO/100 mL H<sub>2</sub>O) and a *Solution D* with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in distilled water (0.2317 gr Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/100 mL H<sub>2</sub>O). Both solutions are mixed and the resulting precipitate is filtered.

Five reaction vessels were subsequently prepared following the same thaumasite synthesis process through the *Th series* (total 800 mL of solution in 1 L containers) but 1.00 gr of the ettringite synthesis sample was added on this occasion. The containers were hermetically closed and introduced in the fridge at 5 °C.

Precipitates from both the *Th series* and *Ett series* were taken out of the fridge after timespans of 1 day, 7 days, 2 months, 6 months and 2 years, and later filtered and dried.

The following techniques and methods were applied to characterize the samples and analyze the results:

- SEM-EDX analyses were carried out with a scanning electron microscope Hitachi S3000N model. This microscope has an X-ray detector Bruker brand XFlash 3001 model for microanalysis and mapping.
- XRD of the experimental samples was conducted in a PANalytical X Pert PRO dust diffractometer using K $\alpha$ 1 radiation, a primary focusing monochromator, and an X Celerator detector. 2 $\theta$ / $\theta$  scans were carried out between 4 and 80 °2 $\theta$  with a step size of 0.017 °2 $\theta$  and a measuring time of 50 seconds per step.

In the case of the *Ett series* sample after 2 years, the Rietveld method [20, 21] served to refine the spectrum seeking to accurately determine the cell parameters of thaumasite. Rietveld refinements have been performed considering the 3 identified phases of sample (calcite, thaumasite and sucrose) by means of FullProf software [22].

### 3. Results and discussion

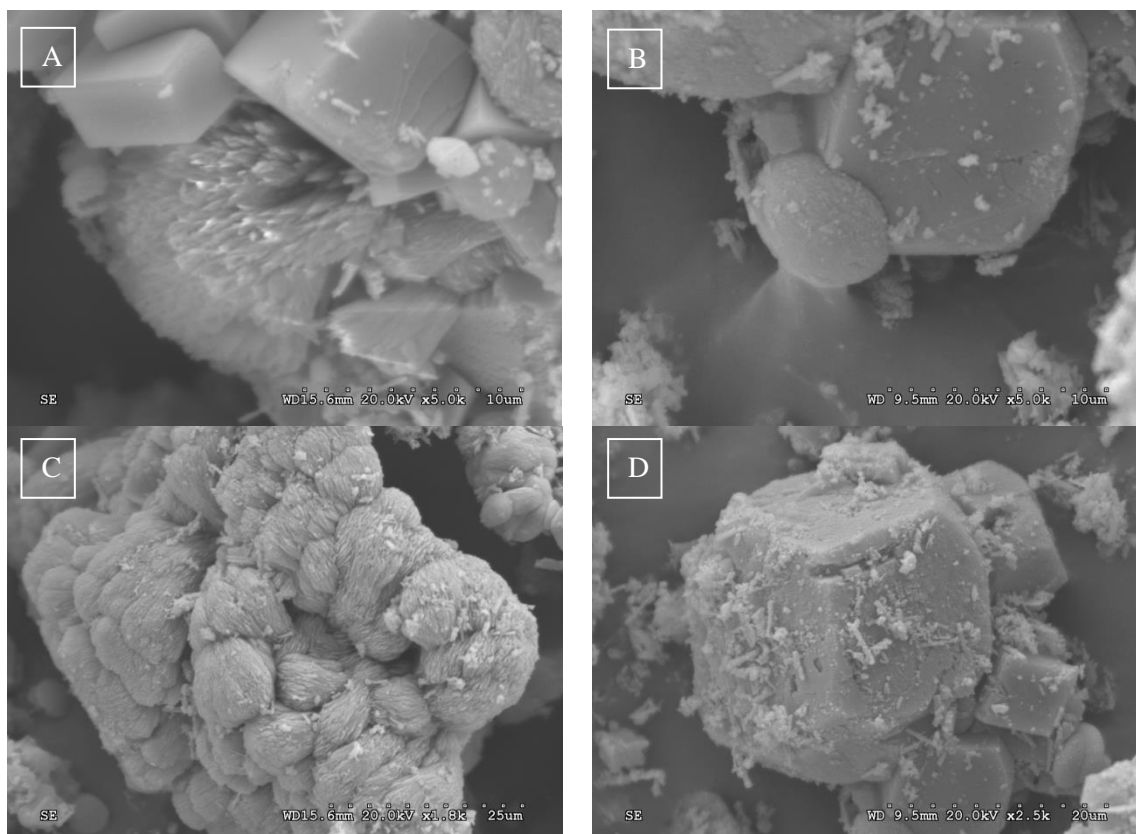
#### 3.1. *Thaumasite synthesis in absence of ettringite. Th series*

The crystalline phases identified by XRD in the samples of the *Th series* after 1 day, 7 days, 2 months, 6 months and 2 years are shown in Table 1. As we can see, only different calcium carbonates are detected during the first two months, namely: calcite  $\text{CaCO}_3$ ; vaterite  $\text{CaCO}_3$ ; and monohydrocalcite  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ ; and thaumasite first appears –together with calcite– after 6 months (Fig. 1d). This is exactly in keeping with the observations of Aguilera *et al.* [14], according to which the *Th series* synthesis experience can be considered finished at that age.

**Table 1.** Identified compounds in the samples of *Th series*.

	Calcite	Vaterite	Monohydrocalcite	Thaumasite
1 day	■	■	■	
7 days	■	■	■	
2 months	■	■	■	
6 months	■			■
2 years	■			■

In Figure 1 the SEM images of calcite, vaterite, the monohydrocalcite and thaumasite are shown. Figure 1 A, B, C show calcium carbonates polymorphs and figure 1D shows the first thaumasite crystals.



**Figure 1.** SEM images of calcite (A), vaterite (B), monohydrocalcite (C) and thaumasite on calcite crystals (D). (A, B, C) at 7 days and (D) at 6 months.

#### 3.2. *Thaumasite synthesis in presence of ettringite. Ett series*

Ettringite was first synthesized by using the method of Cody, Lee [19] described above. The resulting product was analyzed by XRD, and a concentration of 56% for ettringite and 44% for calcite was

obtained after applying the values of the  $I/I_c$  constant for ettringite (2.3) and calcite (3.2) published by International Center for Diffraction Data [23].

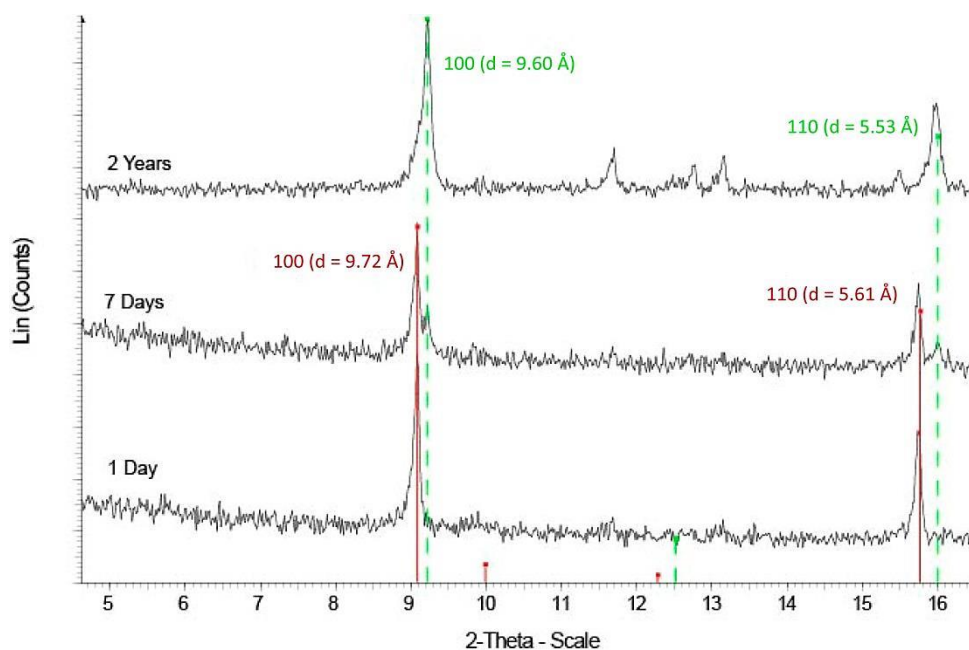
In Table 2 are represented crystalline phases identified by XRD of the *Ett* series samples obtained at timespans of 1 day, 7 days, 2 months, 1 year and 2 years. We can see that after 7 days ettringite has become thaumasite and at 2 months ettringite has disappeared transformed into more thaumasite crystals. The vaterite transforms into a more stable polymorph (calcite).

**Table 2.** Identified compounds in the samples of *Ett series*.

	Calcite	Vaterite	Ettringite	Thaumasite
1 day				
7 days				
2 months				
6 months				
2 years				

### 3.3. Ettringite-thaumasite relation

Figure 2 provides the 5-17  $^{\circ}2\theta$  zones of the three diffractograms for the *Ett series* which best explain the ettringite-thaumasite relation: 1 day, 7 days and 2 years.



**Figure 2.** Diffractograms of *Ett series* at 1 day, 7 days and 2 years. The peaks belonging to ettringite and thaumasite are shown in red and green respectively. Principal reflections and d-spacing values of principal peaks are also shown.

To check whether the thaumasite obtained at the end of the process of *Ett series* is a pure compound, or whether it is an end member of the thaumasite-ettringite solid solution, a refinement of the cell parameters of the sample at 2 years was made by using the Rietveld method. **Table 3** shows the cell parameters values of thaumasite obtained at 2 years in *Ett series*. The parameter "a" value turns out to be situated below 11.11 Å which could correspond to a thaumasite-ettringite solid solution compound [24].

**Table 3.** Refinement of cell parameters of the thaumasite detected in the mortar sample and thaumasite synthesized after 2 years of reaction

Thaumasite	a (Å)	b (Å)	c (Å)	$\alpha$	$\beta$	$\gamma$	Vol (Å) <sup>3</sup>
PDF 24-0038	11.04	11.04	10.39	90	90	120	1096.691
Refined	11.0717 ±	11.0717 ±	10.4451 ±	90	90	120	1108.84
Spectrum	0.0009	0.0009	0.0014				±0.0020

#### 4. Conclusions

The following three conclusions can be drawn from the experimental work described in the present paper:

- 1) The thaumasite synthesis in absence of ettringite demonstrates that this phase appears after 6 months. This means that it can precipitate directly from its components in solution. However, it must not be forgotten either that this is a laboratory experience –using pure reagents in very specific concentrations– and also that such conditions can hardly be found in real concretes.
- 2) Focusing on the *Ett series* allows us to see how thaumasite appears in the presence of ettringite after only a few days (both phases can be seen in the XRD spectrum after 7 days). That proves the catalyzing effect of ettringite.
- 3) Subsequently, ettringite disappears after 2 months in the *Ett series*, and the analytical results of samples obtained after 2 years through the refinement of thaumasite cell parameters would suggest that thaumasite is formed as a result of an ettringite transformation or conversion through the replacement of aluminum atoms with silicon atoms using a solid solution of both.

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