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Thaumasite formation in sugary solutions: Effect of temperature and sucrose concentration

S. Martinez-Ramirez [a,b,*], M.T. Blanco-Varela [b], J. Rapazote [c]

[a] Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), C/Serrano Galvache 4, 28033 Madrid, Spain
[b] Instituto de Estructura de la Materia (CSIC), C/Serrano 121, 28006 Madrid, Spain
[c] Universidade de Trás-os-Montes e Alto Douro, Escola de Ciência e Tecnologia, Departamento de Engenharias, 5000 Vila Real, Portugal

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ABSTRACT

Thaumasite formation in cementitious environments is attributed to sulphate attack (internal or external). Thaumasite is characterized by the presence of octahedrally coordinated silicon, but is formed from the silicate phases of cement, (mainly C–S–H gel), whose silicon atoms are tetrahedrally coordinated. Thaumasite formation is favoured at low temperatures and from recent studies sugar solutions increases calcium solubility and also increases the velocity of formation of thaumasite. The aim of the present study is to explore the effect of temperature (5 °C and 25 °C) and sucrose concentration (5%; 10% and 20% wt) on thaumasite formation from lime and sodium carbonate, sulphate, silicate sugary solutions. Precipitates formed different ages were characterized by XRD and FTIR. At 5 °C larger proportions of thaumasite were formed in 10% sucrose however at 25 °C, the 20% sugary solution generates more thaumasite at shorter times.

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1. Introduction

Thaumasite formation in cementitious environments is attributed to sulphate attack by ions either external to or existing internally in the material. Initially, thaumasite formation is associated with sulphate attack under harsh temperatures (under 15 °C, and particularly between 0 and 5 °C) and high relative humidities [1,2]. Recently, however, thaumasite has been reported to appear at ambient temperature, in both laboratory tests and real situations [3].

Thermodynamically speaking, the carbonate, sulphate and silicate concentrations and pH at which thaumasite is stable in the $CaO–SiO_2–CO_3^{2-}—SO_4^{2-}–H_2O$ system are known values [4], and the salt is also known to be stable across a wide range of calcium concentrations (1–33 mmol/kg).

It seems that quantity, structure and composition of C–S–H gel [5] as well as C_3S/C_2S ratio [6] can play important role in thaumasite formation. A recent experimental study [7] on the effect of calcium hydroxide on thaumasite formation confirmed the importance of that compound in the process. Samples having C–S–H gels with a high C/S ratio and therefore high calcium hydroxide content are more liable to form thaumasite than samples whose C/S ratio is low and excess calcium hydroxide content nil.

Thaumasite is characterized by the presence of octahedrally coordinated silicon, but is formed from the silicate phases of cement, primarily from C–S–H gel, whose silicon atoms are tetrahedrally coordinated. No information is presently available on the evolution from one to the other environment. Two of the variables that can be explored when studying thaumasite formation are calcium solubility in the medium and the effect of temperature [8]. According to Pipilikaki et al. [9] thaumasite formation is evident for mortars (with and without limestone) immersed in Na_2SO_4 solution at 5 °C; however if the same mortars are immersed in the sodium sulphate solution at 20 °C, remain intact.

It is well known that thaumasite formation is favoured at low temperatures, for according to the Kleber's rule, low temperatures contribute to higher degrees of coordination [10,11]. In other words, low temperatures would further the expansion to octahedral coordination. Moreover, low temperatures would also enhance calcium solubility.

Calcium solubility is known to increase in sugary solutions [12] and the most recent studies on thaumasite synthesis used such solutions. Some authors have attempted to obtain thaumasite with mole to mole reactions of $Ca(OH)_2$, $CaCO_3$, amorphous SiO_2 and gypsum [13] or via the interaction of calcium silicates ($CaOSiO_2$, Ca_3SiO_5 and β-Ca_2SiO_4) with $CaSO_4·2H_2O$ and $CaCO_3$ or in excess water, or at a low ambient temperature [14]. Using these methods, calcium salts appeared with the thaumasite in the end product. Other methods also quoted in the literature aim not to produce high purity thaumasite, but merely reproduce the formation processes occurring in nature in a laboratory environment [15–18].

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* Corresponding author at: Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), C/Serrano Galvache 4, 28033 Madrid, Spain. Fax: +34 915855184.
E-mail address: sagrario@iem.cfmac.csic.es (S. Martinez-Ramirez).

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Struble [19] reported that thaumasite can be synthesized by mixing two previously chilled solutions (at 5 °C), one obtained by dissolving CaO in a 10% sugar solution, and the other by dissolving stoichiometric amounts of Na_2SO_4, Na_2SiO_3 and Na_2CO_3 likewise in a 10% sugar solution [19]. Struble's method entailed two advantages: calcium solubility was higher in the sugary solutions, and the use of sodium salts as the anion source instead of calcium salts reduced the likelihood of the appearance of by-products [12].

Barnett et al. [20], Stronach [21] and Aguilera et al. [22] synthesized thaumasite at 5 °C and with 10% sugary solutions using stoichiometric proportions of the reagents proposed by Struble's method and obtained calcium salts as well as thaumasite as end products. Aguilera et al. concluded that by diluting the reagents, they could lower the presence of the by-products.

They therefore proposed a modified Struble method [22] to enhance the efficiency of thaumasite synthesis with non-stoichiometric amounts of reagents. With this method, which calls for lower than stoichiometric concentrations of carbonate and silicate ions, thaumasite forms much more rapidly and with a lower impurity content. Pure thaumasite was obtained after a reaction time of 15 months.

Although very little is known about polysaccharide structural change in the presence of silicon, the structure of these compounds affects their interaction with silicon. Like calcium solubility, silicon solubility is enhanced by the formation of polysaccharide complexes [23].

The literature contains insufficient information on the effect of the concentration of the sucrose solution and temperature on the rate of thaumasite synthesis, even though their effect on lime solubility is amply understood. The composition of the amorphous precipitate that appears in the first few minutes of synthesis and undergoes variation with time (for it is re-dissolved) to form thaumasite, and the role played by sucrose in this process, are also poorly documented. The primary aim of the present study is to explore the effect of temperature and sucrose concentration on thaumasite formation from lime and sodium carbonate, sulphate, silicate sugary solutions.

2. Experimental

Table 1 shows the concentration of the starting materials used in this paper. The sodium salt sugary solution (Na_2SiO_3, Na_2CO_3, Na_2SO_4) was prepared separately from the CaO sugary solution. Three sugar concentrations were used: 5%, 10% and 20%. The solutions were kept at 5 and 25 °C for 4 h and then mixed and stirred magnetically for 5 min. They were then stored at the working temperature (5 or 25 °C) for 1, 2, 6, 12 and 16 weeks.

At the end of each test time, the samples were filtered and precipitates analyzed with XRD and FTIR.

The same concentrations of sodium silicate, sodium sulphate, sodium carbonate and CaO were used in water at 5 °C. The samples were filtered at same ages that in samples prepared in sugar solutions and the solid was analyzed with FTIR. In the present work only three ages were selected (1 day, 3 weeks and 6 weeks) in order to show differences in both solutions.

The 0.18 M CaO and 10% (wt) sucrose solutions were stored at 5 °C for 3 days. The very fine-grained precipitate that formed was filtered and subsequently characterized by XRD and FTIR.

FTIR spectra were obtained on a Thermo Scientific Nicolet 600 spectrometer. Specimen were prepared by mixing 1 mg of sample in 300 mg of KBr. Spectral analysis was performed over the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

A Bruker D8 Advance X-ray diffractometer, consisting of a high voltage, 3-kW generator and a (1.54-Å Cu Kα) copper anode X-ray tube normally operating at 40 kV and 50 mA, was used for the

Table 1
Composition of the starting solutions.

	[Na_2SiO_3·l,5H_2O] (M)	[Na_2CO_3] (M)	[Na_2SO_4] (M)	[CaO] (M)	[Sucrose]
Suc 5%	0.024	0.03	0.10	0.18	5 g suc/95 ml H_2O
Suc 10%	0.024	0.03	0.10	0.18	10g suc/90 ml H_2O
Suc 20%	0.024	0.03	0.10	0.18	20 g suc/80 g H_2O

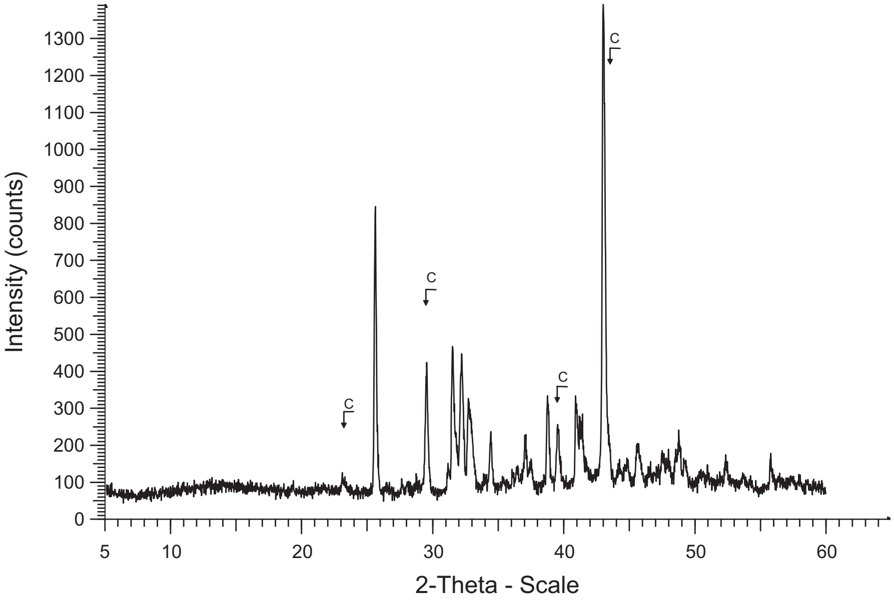

Fig. 1. XRD for the precipitate from CaO – 10% sucrose solution C = calcite.

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