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Formation of thaumasite in carbonated mortars

J. Aguilera, S. Martínez-Ramírez, I. Pajares-Colomo, M.T. Blanco-Varela *

Instituto Eduardo Torroja de Ciencias de la Construcción, CSIC, C/Serrano Galvache s/n, 28033 Madrid, Spain

Abstract

The main objective of this study was to investigate the formation of thaumasite in carbonated Portland cement mortars. Another important purpose was to study the role that ettringite (AFt) plays in the process of formation of Th and its influence in the deterioration of the mortars.

Work was carried out with mortar prisms, elaborated using two different cements: one of them with low Al_2O_3 content (exempt of C_3A) and the other one with high Al_2O_3 content. Additions of different amounts of gypsum and/or calcium carbonate were also done. After three months of curing at 21 °C and 100% RH mortars were submitted to an accelerated carbonation process until total transformation of $Ca(OH)_2$ into $CaCO_3$.

Then mortar prisms were partially immersed in distilled water and kept at temperature ranging from 0 to 5 °C for one year. A mineralogical, micro-structural and physical characterisation was carried out on samples at different ages.

The thaumasite formation rate was much lower in those mortars elaborated with the cement exempt of C_3A than in those mortars made with the cement having high proportion of C_3A when they are conserved in water. The study of transversal sections of prisms reveals the presence of a white expansive product (thaumasite) not always homogeneously distributed.

Keywords: Thaumasite; Mortars durability; Sulfate attack

1. Introduction

Decay of concrete as a consequence of thaumasite formation is shown by experimental evidence, however several aspects of such process remain unclear. There are experimental evidences which support two points of view about the mechanism of thaumasite formation: the first one is that formation of thaumasite occurs as a consequence of the evolution of ettringite when it incorporates Si^{4+} (in octahedral co-ordination) into its structure, substituting the Al^{3+} ions [1–10]; the second one maintains that thaumasite formation is the result of the interaction between sulfates and carbonates (present in the aqueous phase of the cement) and C–S–H gel [9,11–13].

Then, thaumasite has been found in decayed concrete specifically designed to resist sulfate attack [12,14] and also in concrete elaborated with ordinary Portland cement [9,13,15,16], however the relationship between the C_3A content of the cement and the amount or the rate of thaumasite formation are not known. Influence of carbonation degree of concrete on the thaumasite formation has not been studied yet.

Additionally neither the relation between the amount of thaumasite formed and the reduction of concrete strength, nor the exact threshold necessary for a complete breakdown of a mortar or concrete is known [14].

The quantitative determination of thaumasite through XRD, in deteriorated concrete, may be difficult due to the small amount of thaumasite and the structural similarity of thaumasite and ettringite [4,17].

According to Skibsted et al. [18] thaumasite can be clearly quantified in mortars and concrete even in presence of ettringite using $^{29}Si[^1H]$ CPMASNMR technique, when it is in 2–15 wt.% concentration range.

The main objective of this study is to investigate the formation of thaumasite in fully carbonated Portland cement mortars. Another important purpose of this work consists in studying the role that ettringite (AFt) plays in the process of formation of Th and its influence in the deterioration of the mortars.

* Corresponding author. Tel.: +34-91-3020440; fax: +34-91-3026049.

E-mail address: blancomt@ietcc.csic.es (M.T. Blanco-Varela).

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2. Experimental methodology

Chemical analyses of the two different cements are given in Table 1. Cements were mixed with gypsum or calcite, giving four different binders for each original cement:

Type 1 = cement,
Type 2 = cement + 5% gypsum,
Type 3 = cement + 10% gypsum,
Type 4 = cement + 5% gypsum + 10% calcite.

Fifty mortar prisms (1 × 1 × 6 cm) were made with each binder. The water/cement ratio and binder/sand ratio was respectively 0.7 and 1/3. Samples were cured at 21 °C and 100% RH for three months until total hydration of C_3S. Later, they were submitted to an accelerated carbonation process until total transformation of $Ca(OH)_2$ into $CaCO_3$. Once this process was done, the mortars were partially immersed in distilled water and kept at temperature ranging from 0 to 5 °C.

A mineralogical (XRD), micro-structural (SEM–EDX) and mechanical characterisation was carried out on samples after the following periods: end of hydration, end of carbonation, every two months after the immersion in H_2O at 0–5 °C.

The amount of thaumasite was determined in high alumina type 3 mortar soaked for nine months, by applying the Rietveld method to its XRD pattern. The XRD pattern was recorder on a Siemens D500 $\theta/2\theta$ diffractometer (flat reflection mode) by using $CuK\alpha_{1,2}$ radiation, 1.542 Å with a secondary curved graphite monochromator. The sample was loaded in a metacrilate holder by gently sample-front pressing. The 2θ range was 10–70°, in 0.03° steps, counting 20 s/step. The holder was spun during data collection.

The powder pattern type 3 mortar was analysed by the Rietveld method [19] with the GSAS suite of programs [20] by using the pseudo-Voigt peak shape function corrected for axial divergency. ICSD standard pattern for quartz, calcite, thaumasite, gypsum and C_2S were used as reference. In the refinement the overall parameters (background function coefficients, zero error, lattice parameters, profile shape and peak width parameters) were varied and the phase scale factors were optimised.

3. Results and discussion

3.1. Cement with high C_3A content

In Fig. 1 the mean value of mechanical strengths (flexural and compressive) for the different types of mortars, are given.

It is worth to point out, that the addition of 5% gypsum to cement involves the increase of strengths by increasing AFt percentage after the hydration process. On the other hand, higher amount of gypsum added causes a fall of mechanical strengths. The combined addition of gypsum and calcite in mortars type 4 causes the decrease of the resistances in relation with those showed by the mortars type 1. As a general rule it can be said, that carbonation involves the increase of mechanical strengths due to the transformation of portlandite to calcite.

According to DRX results decomposition of the AFt took place in the carbonation step, mainly in the type 3 mortar. In DRX patterns of mortar type 1, the AFt

Table 1
Chemical analyses of the two cements

	LOI	IR	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
$Al_2O_3\downarrow$	1.66	0.57	20.44	3.07	4.08	66.43	0.94	2.9
$Al_2O_3\uparrow$	2.88	0.53	19.68	6.01	1.57	63.30	1.99	3.2

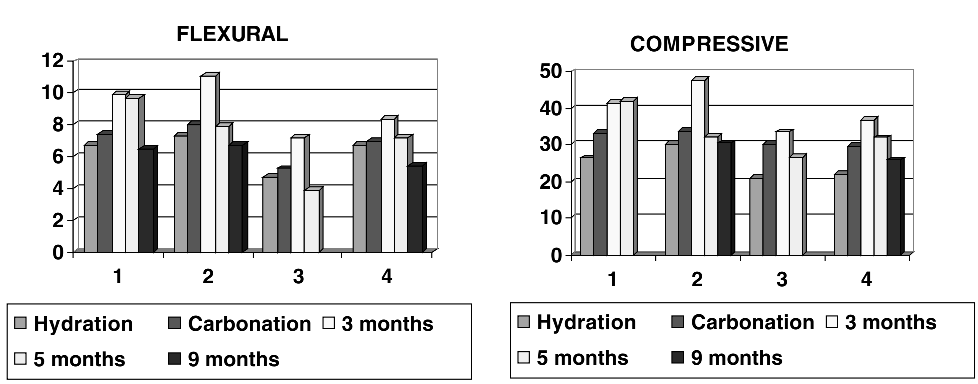

Fig. 1. Mechanical strengths of the cement mortar with high Al_2O_3 content.

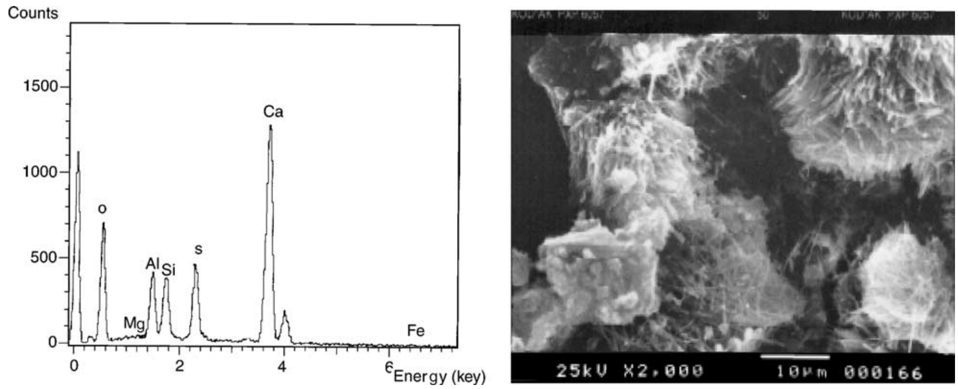

Fig. 2. High alumina type 3 mortar, soaked in water for five months. Micrograph and EDX pattern of acicular crystals.

reflections did not disappear and small peaks due to portlandite remain after carbonation process.

After three months of soaking in H_2O, the main effect observed in samples was the increases of the carbonation, and the increases of mechanical strengths. New AFt or thaumasite formations were not observed through XRD.

Mechanical strengths fell down in mortars type 2, 3 and 4 after five months in water. In mortars type 3, a fall of mechanical strengths (until the 50% of the original) is observed. DRX patterns show the formation of AFt or thaumasite. SEM/EDX studies showed the presence of acicular shape crystals which EDX analyses are given in Fig. 2. The amount of Al and Si in EDX patterns could suggest the existence of ettringite–thaumasite solid solution in the samples, however, due to the small size of the needles, the analysis could also correspond to a mix of thaumasite and ettringite.

After nine months, strengths showed a strong fall in type 4 mortars while type 3 prisms were completely destroyed. Thaumasite was identified through XRD in types 3 and 4. It is worth to point out that in types 3 and 4 mortars a white phase grew inside prisms occupying the whole central part of the specimens which can be observed even at first sight (Fig. 3). In Fig. 4 it is seen how the mortars have broken down through an expansion mechanism.

Through SEM that white phase was seen as a group of needles (Fig. 5), in which analysis revealed almost the total absence of aluminium and therefore confirming thaumasite was the cause of expansion.

The XRD Rietveld plot is displayed in Fig. 6 with the observed (crosses), calculated (line) and difference (bottom line) powder pattern. The refinement converged to $Rwp = 15.5$ and $Rp = 11.4$ indicating a good pattern fitting. The 2θ range between 10–20° was excluded to assure that all the radiation was incised in the sample. The refined weight fractions from this analysis and the derived elemental composition are given in Table 2.

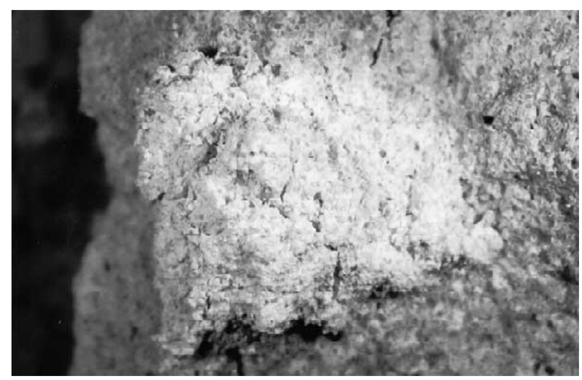

Fig. 3. High alumina type 3 mortar, soaked in water for nine months. White phase in inner part of the prisms.

Fig. 4. High alumina type 3 mortar, soaked in water nine months. Mortar broken down through expansion mechanism.

To analyse this data we have to take into account that they are referred to 100% of the crystalline fraction of the sample, in such a way that amorphous phases (as CSH gel or amorphous aluminate) are not considered.

The acidic insoluble residuum of sample is of 60% and assuming this residuum as quartz (sand), it is

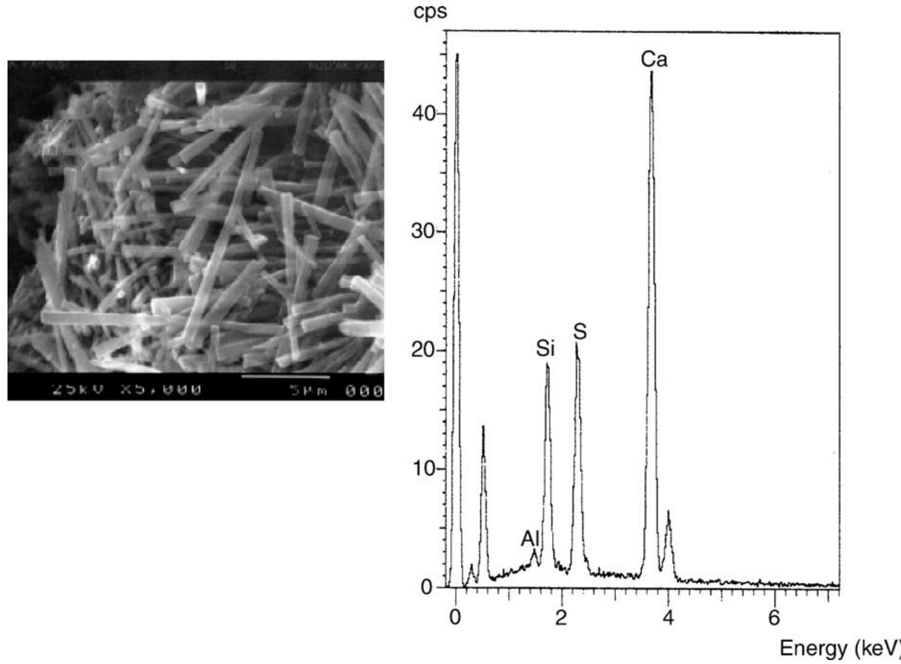

Fig. 5. High alumina type 3 mortar, soaked in water for nine months. Microphotograph and EDX of thaumasite needles.

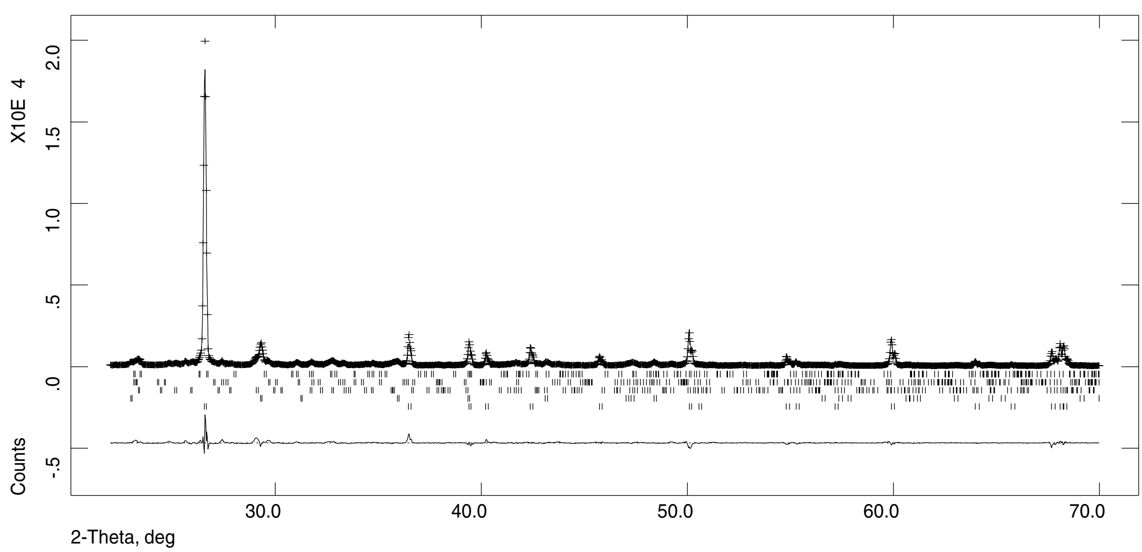

Fig. 6. The mark correspond to the Bragg peaks of the different phases; from bottom to top: quartz, calcite, thaumasite, gypsum and belite monoclinic.

Table 2
Phase composition for the mortar from Reitveld Refinement and corrected

Phase	Quartz	Calcite	Thaum.	Gypsum	C_2S	Amorphous
% wt. Reitveld	75.1	10.8	9.2	2.4	2.5	
% corrected	60	8.6	7.4	2	2	20%

possible to correct the quantitative composition (Table 2). As the initial ratio binder sand was 1/3 and the binder contained 10% of gypsum added, the total amount of silica in sample will be around 3.6 while the silica in thaumasite structure will be of 0.7%. This means that the silica used in the formation of expansive thaumasite is about 20% of the silica of the cement in the binder.

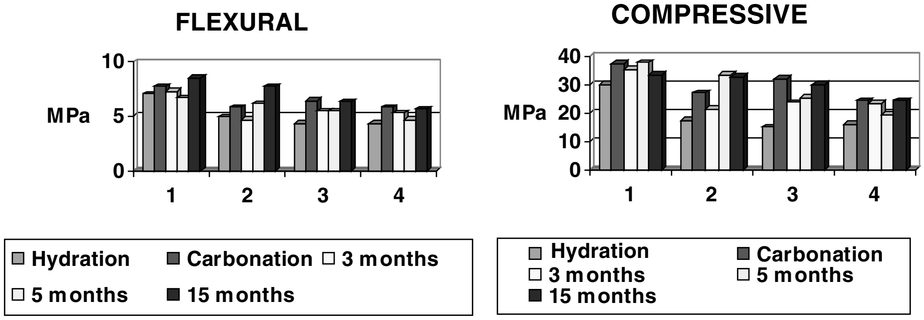

Fig. 7. Mechanical strengths of the cement mortar with low Al_2O_3 content.

3.2. Cement without C_3A

Flexural and compressive strength are shown in Fig. 7. The addition of gypsum causes a slight fall in mechanical strength. The addition of $CaCO_3$ also causes a fall in the mechanical strength although of smaller intensity.

The carbonation causes an increase of the mechanical strength. This increase is caused by the portlandite transformation into calcite. Gypsum is also slightly decomposed due to carbonation. The storage of the specimens in H_2O at temperature ranging from 0 to 5 °C, does not cause significant changes in the mineralogical composition (XRD), only a slight decrease in the mechanical strength is observed after three months, and no variation or even increase in the mechanical strengths at later ages.

The mortars were characterised by means of SEM/EDX after each process was carried out in order to confirm the possible presence of Th in some of the samples. In all samples different morphologies of C–S–H gel were observed as well as the massive presence of calcite crystals as a consequence of carbonation.

Some needles were observed in mortars after being soaked at 0–5 °C for five months (Fig. 8) but not clear evidences of massive thaumasite formation.

Finally it should be mentioned that only low alumina type 1 mortar, underwent an expansive process after 36 months being partially immersed in water (Fig. 9).

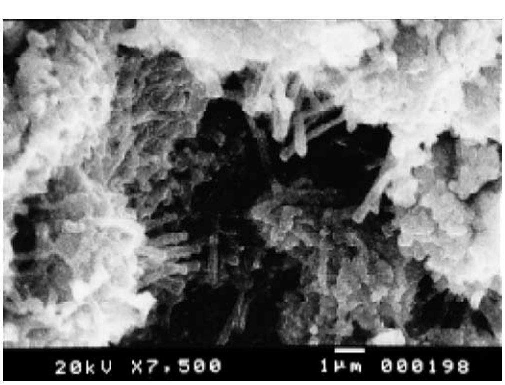

Fig. 8. Low alumina type 1 mortar soaked in water for nine months. Microphotograph of acicular shaped crystals.

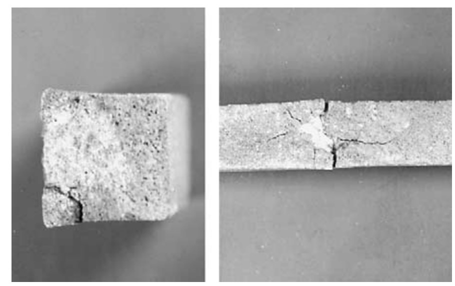

Fig. 9. Low alumina type 1 mortar, soaked in water for 36 months. Mortar broken down through expansion mechanism.

4. Summarizing results

The amount of calcium aluminate in the cement appeared to be a very important parameter that influences the formation of thaumasite in carbonated hydraulic mortars. Thaumasite is formed in mortars made with cement exempt of C_3A but its formation rate is very much lower in this case than in those mortars made with cement having high proportion of C_3A. The formation of the thaumasite in carbonated mortars made with cement having high proportion of C_3A seems to pass through the following stages: (a) decomposition of ettringite due to the CO_2 action, (b) formation of solid solution ettringite–thaumasite or a mix of thaumasite and ettringite, (c) transformation of the ettringite–thaumasite solid solution or of the ettringite in almost pure thaumasite.

Similar decay of mortars due to expansive processes was observed in mortars elaborated with cement in which C_3A was absent as in those made with cement having high proportion of C_3A. Quantitative analysis of XRD patterns through Rietveld method could be an efficient tool to quantify the thaumasite content of mortars and concretes.

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