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Procedure of synthesis of thaumasite

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Abstract

In this work, synthesis procedures to obtain thaumasite were revised. Synthesis of thaumasite applying Struble's method (mix of two cold sugary solutions containing CaO and $Na_2SiO_3 + Na_2SO_4 + Na_2CO_3$, respectively, in stoichiometric proportions) was carried out. Amorphous calcium carbonates and calcium silicate hydrates (intermediate products) were obtained at the very beginning stages of the reaction, which evolved with time forming thaumasite. Thaumasite polluted by calcite and calcium silicate hydrate was obtained after 2 years of reaction. Pure thaumasite was obtained when initial solutions contained less sodium carbonate and sodium silicate than the stoichiometric proportions. The synthesized thaumasite was characterized by X-ray diffraction (XRD), FTIR, SEM/EDX, and NMR. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thaumasite synthesis; Sulfate attack; Cement

1. Introduction

Thaumasite formation in mortars and concrete is nowadays an interesting subject of research because of the lack of basic knowledge on that product [1,2]. Among the items not studied yet, the following could be mentioned: the pH stability of thaumasite, compatible phases with thaumasite in the system in which Portland cement-hydrated phases are found, compositional limits of the aqueous phase at which the mentioned compound is stable etc. In order to determine the stability conditions of thaumasite by thermodynamic calculations, it is necessary to know the exact solubility product of the compound, therefore, pure thaumasite has to be synthesized. The main objective of this work consists of the synthesis of pure thaumasite.

An overview on the bibliography published about thaumasite synthesis makes us remark that most of the authors agree in some points about the conditions under which the synthesis must be accomplished:

(i) *Temperature:* a range of 0–5°C is preferred for these 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 $[Si(OH)_6]^{2-}$ [3].
- Low temperatures favor the solubility of the calcium salts necessary for the synthesis [4] (this particular point is not shared by Bensted and Varma [5] who warns that just $Ca(OH)_2$ is more soluble at low temperature).

(ii) *Humidity:* a high humidity level allows the transportation of the ions needed for the synthesis: SO_4^{2-} and CO_3^{2-} [3].

(iii) *Time:* a long time. Thaumasite synthesis is a long process that involves the expansion of the Si coordination sphere [3].

Some authors tried to obtain thaumasite by interaction of different calcium silicates ($CaOSiO_2$, Ca_3SiO_5, and β-Ca_2SiO_4) with $CaSO_4{\cdot}2H_2O$ and $CaCO_3$ in an excess of H_2O, at low ambient temperature [6]. X-ray diffraction (XRD) analysis of obtained samples warned of a possible contamination with calcite and aragonite [7]. Also, some thaumasite is obtained by mole to mole reaction of $Ca(OH)_2$, $CaCO_3$, amorphous SiO_2, and gypsum, maintaining the system at 5°C for 4 months [4]. With this method, calcium salts appear in the final products together with thaumasite.

There are other methods (quoted in literature) that do not aim to produce high-purity thaumasite, but just to repeat in the laboratory the formation processes occurring in nature; for example, mixing H_2O, portlandite, calcite (or atmo-

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Table 1
Concentration of reagents used in the synthesis

	Concentration of solutions (molar)		
Sample	CaO	$Ca(OH)_2$	$Na_2SiO_3 + Na_2SO_4 + Na_2CO_3$
1	0.06		0.02
2	0.03		0.01
3	0.099		0.033
4		0.06	0.02
5		0.03	0.01

spheric CO_2), gypsum, and colloidal silica. Good results are not obtained unless the silica gel contains a minimum of 1% of alumina [8]. The author suggests, in order to obtain good results in 2 weeks, it is necessary to maintain high humidity levels at temperatures of about 4°C, to maintain the presence of sulfate and carbonate ions, and to add a content of alumina in the starting reactants of about 0.4–1%. This method involves the utilization of alumina as a precursor of thaumasite growth. There are some works relating to this idea, i.e., Crammond and Nixon [9] who proposed the use of Mg as a kind of catalyst, because it might form magnesium silicate hydrate, that would act as intermediate product and would stimulate the growth of thaumasite.

Bensted [3] obtained thaumasite by reaction between the calcium silicate hydrate (formed at the time of hydration of alite — Ca_3SiO_5 — and belite — Ca_2SiO_4) and an aqueous solution containing $SO_4{}^{2-}$ and $CO_3{}^{2-}$. Kollman et al. [10] mixed Portland cement clinker (acting as supplier of Si^{4+}) with $CaCO_3$ (or atmospheric CO_2) and gypsum in water at 2°C; initially, ettringite was formed but after 40 days this phase was transformed into thaumasite. Bensted [3] also obtained thaumasite by reaction of AFt phase: $C_6[(Al,Fe)(OH)_6]_2(SO_4)_3{\cdot}26H_2O$ with C-S-H gel and carbonate ions in sugary solution. This method is based on the Al–Si ions exchange previously demonstrated by Baronio and Berra [11].

Thaumasite can be obtained by mixing two solutions previously cooled at 5°C: The first solution is obtained by dissolving CaO in a 10% sugar solution. The second one contains Na_2SO_4, Na_2SiO_3, and Na_2CO_3 in H_2O. Stoichiometric amounts are used [12]. With this method, published by Struble [12], two advantages are obtained: the increase of calcium solubility due to the use of sugary solutions and the use of sodium salts as the anion source instead of calcium salts, which reduces the probability for secondary products to appear [13].

2. Experimental

The following investigations were carried out in order to get pure thaumasite:

(a) thaumasite synthesis according to Struble's method [12],
(b) study of the stages through which synthesis runs,
(c) new synthesis method.

2.1. Thaumasite synthesis according to Struble's method

The synthesis procedure carried out at the laboratory consisted of mixing two sugary solutions (10 wt.%) that were cooled at 5°C. The first solution contained CaO or $Ca(OH)_2$, so it contributed Ca^{2+} ions; the second one had Na_2SiO_3, Na_2SO_4, and Na_2CO_3 thus contributing the $SO_4{}^{2-}$, $CO_3{}^{2-}$, and $SiO_3{}^{2-}$ ions necessary for the reaction. Stoichiometric relations according to the following reaction were used:

$$SiO_3^{2-} + SO_4^{2-} + CO_3^{2-} + 3Ca^{2+} \xrightarrow{H_2O} CaSiO_3{\cdot}CaSO_4{\cdot}CaCO_3{\cdot}15H_2O$$

Different starting concentrations of reactants were used. The samples so obtained were kept at (0–5°C) and characterized through XRD, FTIR, and SEM/EDX after periods of 2 months starting from the fourth month of initiating the reaction. The concentrations of the solutions as well as the starting reagents are given in Table 1.

2.2. Thaumasite synthesis stages

When the sugary mixes of CaO and $Na_2SiO_3 + Na_2SO_4 + Na_2CO_3$ are put in contact, a cloudiness takes place and a precipitate is formed. So, a study of the products formed in Sample 2, after 5 min, and after 1 and 7 days of reaction, was carried out by XRD and FTIR.

2.3. New synthesis method

A modification in Struble's synthesis procedure was tested [12]. Those reaction conditions generally accepted in the bibliography (low temperature, high level of humidity, and long time of reaction) were maintained. The starting products used (calcium oxide and sugary solutions of sodium salts) were the same as in the previous method but the ratios of the used concentrations were modified.

Different dosages were tested, always maintaining the concentration of $SO_4{}^{2-}$ above the stoichiometric value corresponding to those of silicate and carbonate. This is done in order to reach the solubility product of the thauma-

Table 2
Concentration of reagents used in the new synthesis process

		Concentration of solution (M)			
	Sample	CaO	Na_2SiO_3	Na_2CO_3	Na_2SO_4
(CO_3↓, silicate↓)	A	0.05	0.01	0.01	0.0166
(CO_3↓)	B	0.05	0.0166	0.01	0.0166
(CO_3↓, silicate↓↓)	C	0.025	0.006	0.008	0.01
(CO_3↓↓, silicate↓↓)	D	0.025	0.006	0.006	0.01

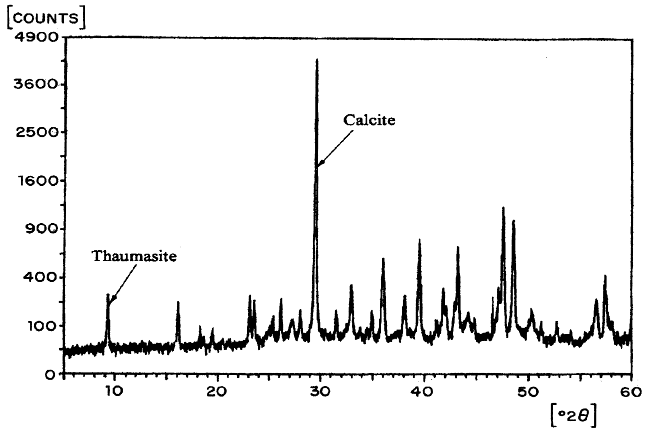

Fig. 1. XRD pattern of Sample 2 after 6 months of reaction.

site by increasing the concentration of SO_4^{2-} (so gypsum, which is quite a soluble product, would be formed) and by diminishing the concentration of the CO_3^{2-} and silicate (they would form calcite and C-S-H gel, which are very insoluble products). In Table 2, the different concentrations of used reagents are detailed.

3. Results and discussion

3.1. Struble's method

After 4 months of reaction, thaumasite crystals were obtained in all the samples. However, together with thaumasite, calcite crystals and amorphous calcium silicate were also observed. In Fig. 1, a diffractogram of Sample 2 is presented. After 6 months of reaction, the diffraction lines belonging to calcite can be observed and also those belonging to thaumasite. The high calcite percentage in the sample is clearly deduced from the X-ray pattern.

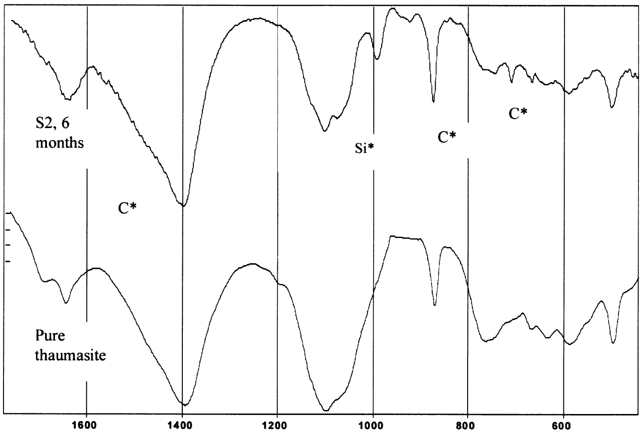

Fig. 2. FTIR spectra of Sample 2, 6 months of synthesis and pure thaumasite. C * = calcite bands; Si * = octahedral Si band.

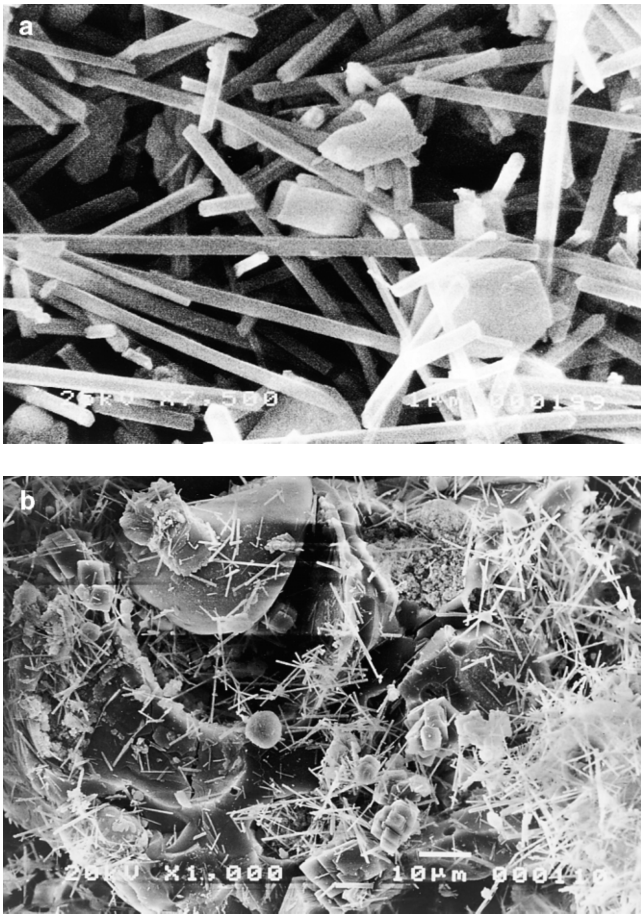

Fig. 3. SEM pictures of Sample 2 (6 months of reaction): (a) thaumasite needles and calcite prisms; (b) thaumasite needles, calcite prisms, and amorphous calcium silicate hydrate.

In Fig. 2, the FTIR spectra belonging to Sample 2 (6 months of reaction) and to pure thaumasite are presented. In the Sample 2 spectrum, the bands belonging to the thaumasite are clearly seen.

Also a group of bands with frequencies of vibration at 1800, 1430, 847, and 712 cm^{-1} can be observed. These bands indicate the presence of calcite in the sample. Finally, the band towards 980 cm^{-1} shows the existence

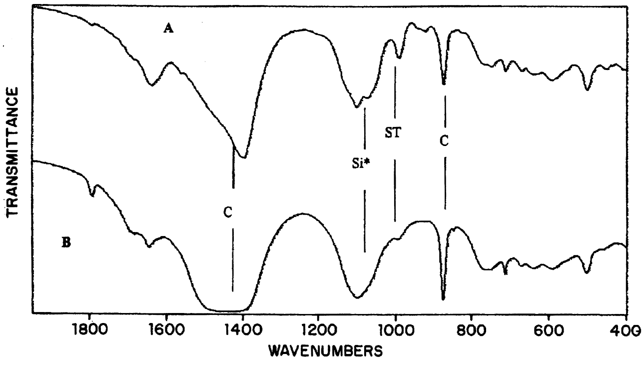

Fig. 4. (A) FTIR of Sample 2 (6 months of reaction, CaO was used as starting material). (B) FTIR of Sample 5 (6 months of reaction, $Ca(OH)_2$ used as starting material). C = calcite; S.T. = tetrahedral silicate; Si * = octahedral silicate.

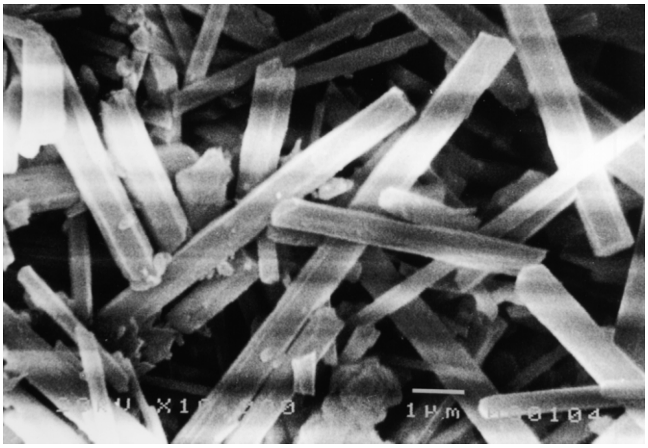

Fig. 5. Microphotograph of Sample 2 (14 months of reaction) where the growth of thaumasite needles is observed.

of an amorphous hydrated calcium silicate having Si in tetrahedral coordination.

The analyses carried out through SEM/EDX confirm the presence of calcite crystals and hydrated calcium silicate together with thaumasite crystals. In Fig. 3, different microphotographs of Sample 2 after 6 months of reaction are shown.

The efficiency of the reaction is higher when CaO solution is used as a reagent rather than $Ca(OH)_2$. In Fig. 4, the FTIR spectra of two samples (Sample 2 was prepared with CaO solution and Sample 5 was prepared with $Ca(OH)_2$ solution), after 6 months of reaction, are presented.

The relative intensity of the calcite/thaumasite bands and hydrated calcium silicate/thaumasite bands is higher in Spectrum B than in Spectrum A, which indicates a higher amount of impurities in the first case.

Through the analyses carried out every 2 months (6, 8, 10 ... months) to the samples, it could be observed that the increase in the time of reaction causes significant changes in the microstructure of the system. In Fig. 5, a SEM picture of Sample 2 (14 months of reaction) can be seen. The increase of the size of the thaumasite crystals is evident.

The thaumasite percentage in the samples increases with time of reaction. Table 3 shows the relative amounts of calcite and thaumasite in the samples in relation with time measured by XRD. The concentration of reagents affects the reaction rate and the amount of calcite and hydrated calcium silicate obtained. Table 3 shows the relative intensity of RX characteristics reflection lines in Samples 1, 2, and 3 after 6 months of reaction; the most diluted solution (Sample 2) has the highest relative amount of thaumasite.

Through FTIR, the increase in thaumasite percentage (increase of the intensities of vibration bands) can be

Table 3
Relative intensity of RX characteristics reflection lines

Samples (date)	Thaumasite $2\theta = 9.14$ (%)	Calcite $2\theta = 29.40$ (%)
1 (4 months)	14	86
1 (6 months)	19	81
2 (6 months)	24	76
2 (10 months)	26	74
3 (6 months)	6	94
3 (12 months)	22	78
4 (10 months)	7	93
4 (24 months)	17	83

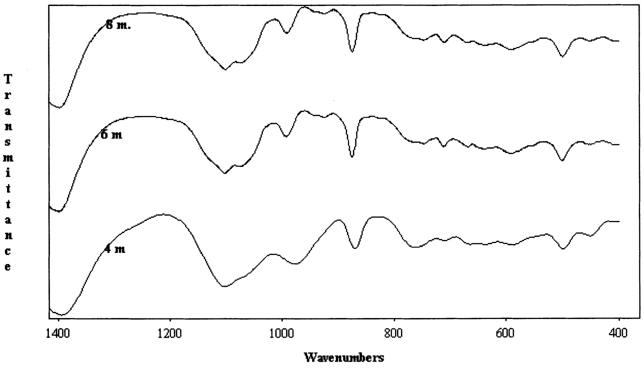

Fig. 6. FTIR of the Sample 3 after 4, 6, and 8 months of reaction.

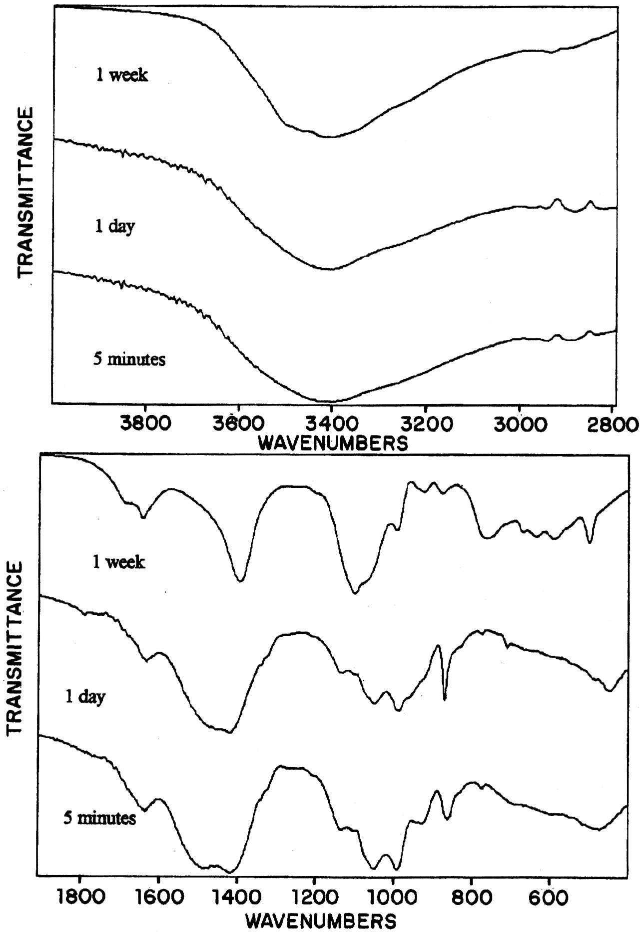

Fig. 7. FTIR of Sample 2 (5 min and 1 and 7 days of reaction).

Table 4
Evolution of composition of samples

Sample (date)	Thaumasite $2\theta = 9.20$ (%)	Calcite $2\theta = 29.40$ (%)
C (3 months)	30	70
C (6 months)	45	55
C (9 months)	75	25
D (3 months)	45	55
D (6 months)	61	49
D (9 months)	93	7

observed. In Fig. 6, FTIR spectra of Sample 3 after 4, 6, and 8 months can be seen.

3.2. Thaumasite synthesis stages

A study of the precipitate formed in Sample 2 after 5 min and after 1 and 7 days of reaction was carried out by XRD and FTIR. The precipitate was amorphous to XRD during the time of the study.

In Fig. 7, the FTIR spectra of precipitates obtained from Sample 2 after 5 min and 1 and 7 days of reaction are presented. The sample obtained after 5 min of reaction presents some broad bands towards 1400–1500 cm^{-1} (tension vibrations due to CO_3^{2-}). The longer the time of reaction, the more centered (towards 1400 cm^{-1}) are the appearance of the bands. An intense band at 1400 cm^{-1} is characteristic of the carbonates in the thaumasite.

In a similar way, in the region of tension vibrations of the SO_4^{2-} group, several bands appear in the spectrum of the sample reacted for 5 min. When increasing the time of reaction, these bands progressively transform into one band centered at 1100 cm^{-1}. This frequency is characteristic of sulfates in the thaumasite.

In the region of vibration of silicates, the most interesting thing to be emphasized is the progressive decrease of the intensity of the band at 970 cm^{-1} (very intense after 5 min of reaction). This band is characteristic of the tetrahedral SiO_4 groups. Through SEM/EDX, the existence of a calcium silicate hydrate was shown after 5 min and 7 days of reaction. When reaction time increases, a band at 1065 cm^{-1} appears, characteristic of octahedral silicates.

3.3. New synthesis method

The new set of experiments shows an important rise in the thaumasite formation rate when the amount of carbonates and silicates used as starting reagents decrease. A study of the evolution of the reaction with time was carried out. In Table 4, the results of semiquantitative analysis based on the study of the intensity of XRD lines are presented. A considerable increase of the amount of thaumasite with time can be observed. Sample D only contains 6 wt.% of calcite after 9 months of reaction.

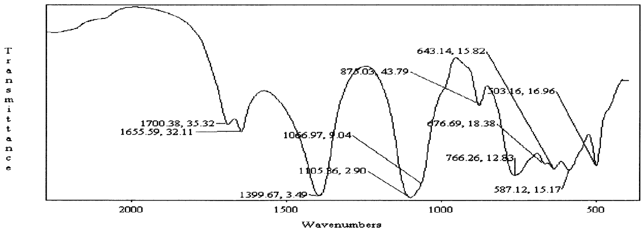

Fig. 8. FTIR of Sample D after 15 months of reaction.

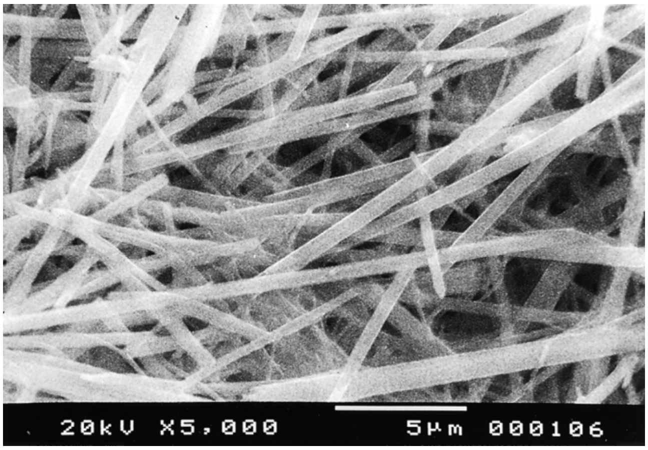

Fig. 9. Sample D, 15 months of reaction. Microphotographs of thaumasite needles.

The XRD pattern of Sample D after 15 months of reaction shows X-ray reflections of thaumasite. Calcite reflections were not observed. The FTIR spectra (Fig. 8) show the thaumasite bands; the vibration bands belonging to hydrated calcium silicate have disappeared.

The pureness of the synthesized thaumasite in Sample D was confirmed through SEM/EDX and ^{29}Si CP MAS NMR. Neither amorphous hydrated calcium silicate nor calcite crystals were detected by the microscopic technique. In Fig. 9, thaumasite needles are observed, but calcite or hydrated calcium silicate is absent.

^{29}Si CP MAS NMR spectrum of the synthesized thaumasite (Fig. 10) shows an unique signal at − 179 ppm. Any

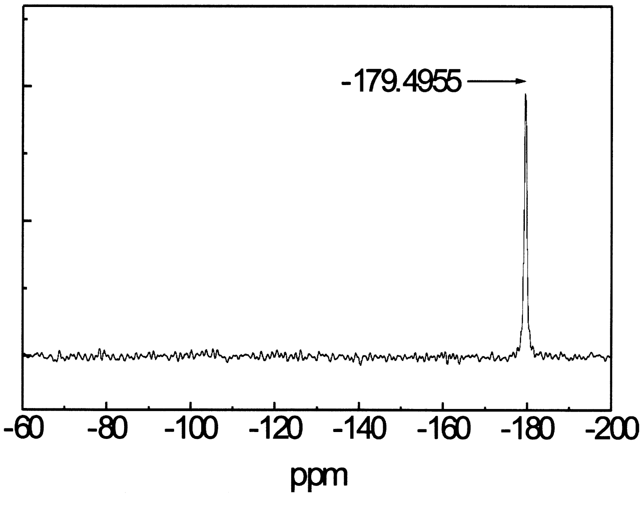

Fig. 10. Sample D, 15 months of reaction. ^{29}Si CP MAS NMR spectrum.

other signal in the chemical shift region of ^{29}Si in tetrahedral coordination (which would have indicated the presence of amorphous hydrated calcium silicate) was not recorded.

4. Concluding remarks

Synthesis of thaumasite was carried out by the method proposed by Struble [12]. Precipitation of amorphous calcium carbonate and calcium silicate hydrate occurs during the first minutes of the synthesis reaction. These intermediate products evolve with time (they are newly dissolved), giving rise to thaumasite formation. If during the synthesis reaction, the amorphous phases grow or crystallize forming big crystals, their specific surface is reduced and their dissolving process becomes slow. This means that the rate of thaumasite formation decreases with time.

The use of stoichiometrical amounts of reagents gives place to the first thaumasite crystals forming after 4 months of reaction, but impurities of calcite and hydrated calcium silicate also appear.

- The increase of the reaction time increases the thaumasite percentage in the sample but at a very slow rate. All the samples, after 24 months of reaction, contained a high percentage of pollutants (calcite and calcium silicate hydrate).
- The more diluted the reagents are then the smaller the percentages of secondary products found.
- The thaumasite/impurities ratio increases when CaO is used as the starting raw material instead of $Ca(OH)_2$.

A modified Struble method [12] has been proposed to improve the efficiency of the synthesis reaction of thaumasite with nonstoichiometric amounts proportions of reagents. In this method, concentrations of carbonate and silicate ions inferior to the stoichiometrical were used. The new synthesis conditions proposed gives rise to thaumasite formation much more rapidly and with a small content of impurities. Pure thaumasite was obtained after 15 months of reaction.

Acknowledgments

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