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Influence of gypsum additive on the formation of calcium silicate hydrates in mixtures with C/S = 0.83 or 1.0

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The influence of gypsum additive on the formation of calcium silicate hydrates and on the formation of a sequence of intermediary compounds in the $CaO–SiO_2·nH_2O–H_2O$ system has been examined. The synthesis was carried out in unstirred suspensions. The molar ratios of primary mixtures were CaO/SiO_2 = 0.83, 1.0 and $SO_3/(SiO_2 + SO_3)$ = 0, 0.0125, 0.025. The durations of isothermal curing at 200 °C were 4, 8, 16 and 72 h. It was established that sulfate ions improve the synthesis of 1.13 nm tobermorite in the $CaO–SiO_2·nH_2O–H_2O$ system with CaO/SiO_2 = 0.83 at 200 °C. However, a larger amount of gypsum ($SO_3/(SiO_2 + SO_3)$ = 0.025) stimulates the formation not only of 1.13 nm tobermorite but also of $CaSO_4$ and xonotlite. In the $CaO–SiO_2·nH_2O–H_2O$ system with CaO/SiO_2 = 1.0, a small amount of sulfate ions prolong the persistence of intermediate compounds – 1.13 nm tobermorite and C–S–H (I). The products of synthesis were characterized by X-ray diffraction analysis, simultaneous thermal analysis and Fourier transform infrared spectroscopy.

Key words: *gyrolite; calcium sulfate; calcium silicate hydrate; X-ray diffraction*

1. Introduction

Significant amounts of sulfate impurities enter almost all carbonate rock. Moreover, large quantities of the by-product, gypsum, are produced by chemical industries and are currently being disposed by dumping into rivers, ponds or landfills. Due to increasing concern about environmental pollution, it is essential to utilize these wastes as building materials. Therefore, sulfate attack in concrete structures is among the major durability concerns in civil infrastructure systems. Proper modelling techniques can help us to understand the influence of severe environments on the properties of concrete, and improve the decision making process in every stage of construction and

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maintenance. It should be underlined that the study of the effect of salt (sulfate, chloride, etc.) on the durability of cement stone is highly relevant in countries with access to the sea, because they have constructions (jetties, quays, etc.) affected by sea water. The main hydration products and principal binding phases in all calcium silicate-based pastes and concrete are calcium silicate hydrate (C–S–H) gels. The composition and the degree of structural order of C–S–H phases depend on the nature of the system. For these reasons, some researchers studied the influence of gypsum additives on the synthesis of calcium silicate hydrate [1–12]. Most of them have found that the addition of gypsum accelerates the formation of calcium silicate hydrates [1–3, 5–8].

Krzheminskiy et al. [2, 3] indicated that at 175 °C, when the molar ratio of the primary mixture is CaO/SiO_2 = 0.5–1.0, small amounts (1–5%) of gypsum stimulate the reaction of CaO with C–S–H (I). Kuatbaev [7] has shown that gypsum has no influence on the solubility of quartz, but gypsum is more soluble than quartz and the solution contains a significant excess of anions. For this reason, SiO_4^{4-} is isomorphically replaced by SO_4^{2-}, and SO_3-substituted calcium silicate hydrates, more soluble than pure compounds, are formed. Grabko [8] found that gypsum additive in mixtures with a molar ratio CaO/SiO_2(C/S) = 0.8 primarily and significantly stimulates the formation of ellastadite. He indicates that calcium silicate hydrates start forming when all the volume of $CaSO_4$ has reacted. In this case, in the products α-C_2S hydrate prevails and during synthesis gradually recrystallizes into SO_3-substituted C–S–H (I), while in the pure system only C–S–H (I) is formed. Even 7% of gypsum can enter into the crystal structure of these compounds. However, after using a larger quantity of this additive, C–S–H (I) is metastable and regroups into 1.13 nm tobermorite. Vektaris et al. [9, 10] have also found that sulfate ions stimulate formation of calcium silicate hydrates. This process is more intensive in mixtures with the molar ratio CaO/SiO_2 equal to 0.8 than in equal to 1.0. Moreover, in the CaO–amorphous SiO_2–H_2O system, 5–10% of gypsum strongly affects the crystallization of C–S–H (I) into 1.13 nm tobermorite.

Other authors [4, 11, 12] indicate however that in lime–quartz–water mixtures under hydrothermal conditions at 175 °C gypsum has no influence on the solubility of lime, but somewhat changes the mineral composition of the final products. Besides, it was estimated that only 1.5% of sulfate ions can enter the calcium silicate hydrate crystal structure.

Thus, there are not much data (and none of it is comprehensive) about the sequence of the newly formed compounds and the influence of gypsum additives on it. The published papers describe the influence of alkaline metals [13–14], aluminium [15–18] and other elements [19–21] on the synthesis and properties of calcium silicate hydrates. Moreover, almost all of these tests were performed with quartz – less active form of SiO_2. There is little data about the effect of a more active form of SiO_2 (amorphous SiO_2) on the synthesis of calcium silicate hydrates or the sequence of the new compounds formed or the influence of additives on these processes.

The main objective of the present work was to examine the influence of gypsum additives on the formation of calcium silicate hydrates in the $CaO–SiO_2{\cdot}nH_2O–H_2O$ mixture with C/S = 0.83 or 1.0 as well as to analyze and explain the formation of a sequence of intermediary compounds.

2. Experimental

The following reagents were used as starting materials: fine-grained $SiO_2{\cdot}nH_2O$ (losses on ignition 21.43%, specific surface area S_a = 1560 m²/kg), calcium oxide (S_a = 548 m²/kg), $CaSO_4{\cdot}2H_2O$ (losses on ignition 23%).

The syntheses of calcium silicate hydrates were carried out in unstirred suspensions in vessels of stainless steel. The molar ratios of primary mixtures CaO/SiO_2 were 0.83, 1.0 and $SO_3/(SiO_2 + SO_3)$ = 0, 0.0125, 0.025. Dry primary mixtures were mixed with water to achieve a water/solid ratio of the suspension equal to 10.0. Hydrothermal synthesis was carried out under saturated steam pressure at 200 °C; the durations of isothermal curing were 4, 8, 16 and 72 h. The products of the syntheses were filtered, rinsed with ethyl alcohol to prevent carbonization, dried at 50 °C ± 5, and sieved through a sieve with a mesh size of 80 μm.

The X-ray powder diffraction (XRD) data were collected with a DRON–6 X-ray diffractometer equipped with the Bragg–Brentano geometry using Ni-filtered CuK_α radiation and a graphite monochromator operating under the voltage of 30 kV and an emission current of 20 mA. The step-scan covered the angular range 2–60° (2θ) in steps of $2\theta = 0.02°$.

Simultaneous thermal analyses (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) were also employed for investigating the thermal stability and phase transformations of the synthesized products at the heating rate of 15 °C/min, the temperature ranged from 30 °C to 1000 °C under air atmosphere. The test was carried out on a STA 409 PC Luxx Netzsch instrument. Ceramic sample handlers and crucibles of Pt–Rh were used.

FTIR spectra were obtained with the aid of a Perkin Elmer FT–IR Spectrum X system. The specimens were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of 4000–400 cm^{-1} with a spectral resolution of 1 cm^{-1}.

The specific surface area of the raw materials was determined by Blaine's method with an air permeability apparatus (Model 7201, Toni Technik Baustoffprufsysteme GmbH).

3. Results and discussion

In the $CaO–SiO_2{\cdot}nH_2O–H_2O$ system in which the molar ratio of the primary mixture of C/S = 0.83 at 200 °C, 1.13 nm tobermorite rapidly forms, because the key

components of this compound (*d* spacing – 1.137, 0.546, 0.306, 0.280, 0.207, 0.184 nm) and C–S–H (I) (*d* spacing – 0.306; 0.280; 0.184 nm) were identified after 4 h of isothermal curing (Fig. 1, curve 1).

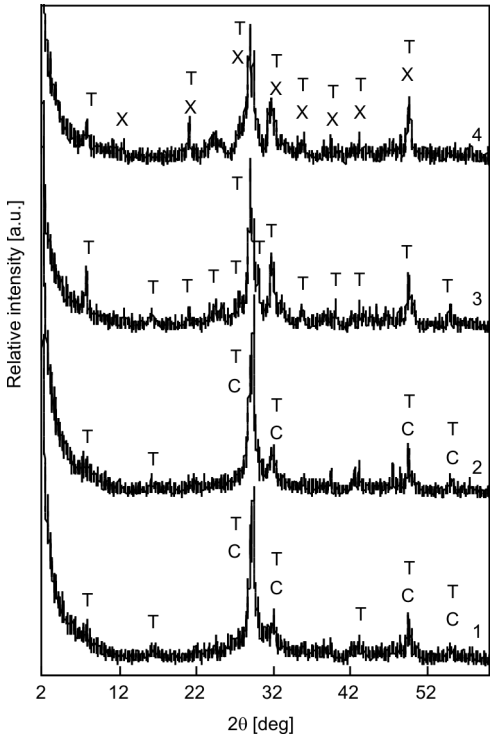

Fig. 1. X-ray diffraction patterns of the products of the syntheses; durations (h) of the hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72; C – C–S–H (I), T – 1.13 nm tobermorite, X – xonotlite

After 16 h of synthesis 1.13 nm tobermorite has crystallised; its characteristic peaks increase (Fig. 1, curve 3). Upon continuing the synthesis, 1.13 nm tobermorite starts to transform into a higher-basicity compound – xonotlite (*d* spacing – 0.779, 0.421, 0.308, 0.282, 0.250, 0.234, 0.204, 0.184 nm) (Fig. 1, curve 4). Thus, at 200 °C 1.13 nm tobermorite is unstable, since after 72 h it starts recrystallising into xonotlite.

The analysis of the influence of gypsum additive on the formation of tobermorite at 200 °C, when the initial molar ratios $CaO/(SiO_2 + SO_3) = 0.83$ and $SO_3/(SiO_2 + SO_3) = 0.0125$ shows that during the first hours sulfate ions accelerate the synthesis of monobasic calcium silicate hydrates.

After 4 h of synthesis 1.13 nm tobermorite (*d* spacing – 1.139, 0.546, 0.307, 0.280, 0.184, 0.167 nm) and C–S–H (I) (*d* spacing – 0.546, 0.307, 0.280, 0.184, 0.167 nm) form in the products (Fig. 2, curve 1). Upon extending the duration of synthesis to 72 h, a higher degree of crystallinity 1.13 nm tobermorite forms in the products because the intensity of the basic peak, characteristic of tobermorite (*d* spacing – 1.13 nm) increases (Fig. 2). Thus, it was established that sulfate ions improve the synthesis of 1.13 nm tobermorite: after 72 h of hydrothermal treatment this compound remains stable, i.e. it does not transform into xonotlite, unlike a pure mixture.

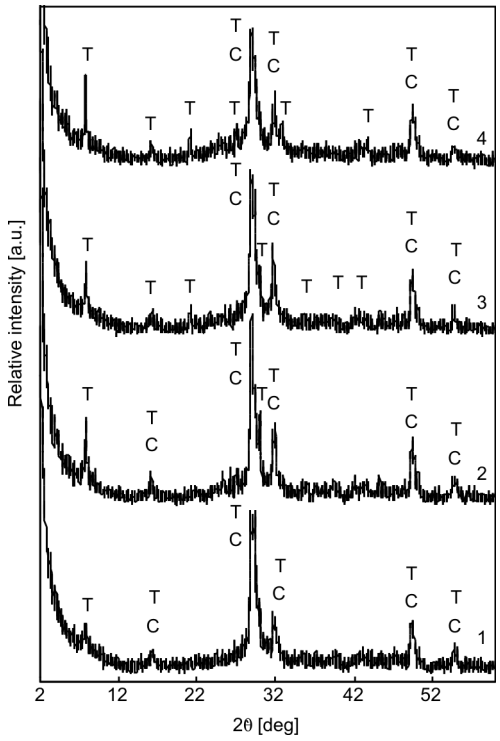

Fig. 2. X-ray diffraction patterns of the products of the syntheses when the molar ratios $CaO/(SiO_2 + SO_3)$ in the primary mixture equal 0.83 and $SO_3/(SiO_2 + SO_3)$ – 0.0125; durations (h) of hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72; C – C–S–H (I), T – 1.13 nm tobermorite

Upon adding a larger amount of gypsum into the mixture ($CaO/(SiO_2 + SO_3)$ = 0.83 and $SO_3/(SiO_2 + SO_3)$ = 0.025), acceleration of the synthesis was noticed. However, after 4 h of hydrothermal treatment not only C–S–H (I) (*d* spacing – 0.307, 0.281, 0.184, 0.167 nm) and 1.13 nm tobermorite (*d* spacing – 1.142, 0.548, 0.307, 0.298, 0.281, 0.224, 0.200, 0.184, 0.167 nm) but also $CaSO_4$ (*d* spacing – 0.350, 0.175, 0.167 nm) formed (Fig. 3, curve 1).

The analysis of the DSC and FTIR results shows that during the first hours of synthesis a fair amount of C–S–H (I) is formed. This is represented by a clear exothermic effect at 851 °C in the thermal analysis curve (Fig. 4a, curve 1). Moreover, the absorption at 3474, 1639, 1492, 971, 674 and 449 cm^{-1} characteristic of C–S–H (I) and tobermorite were identified (Fig. 4b, curve 1).

Upon extending the synthesis to 8 h, the degree of crystallisnity of the formed tobermorite increases because the intensity of the peak of the *d* spacing – 1.13 nm grows in the X-ray diffraction pattern (Fig. 3, curve 2). In the meantime, the amount of $CaSO_4$ decreases, because the intensity of its main peak (*d* spacing – 0.350 nm) decreases. Similar results were obtained after 16 h of hydrothermal treatment (Fig. 3, curve 3). The presence of a low intensity absorption bands at 1201 cm^{-1} and 613 cm^{-1}, as observed in the spectrum, shows the formation of a new compound – xonotlite (Fig. 4b, curve 3).

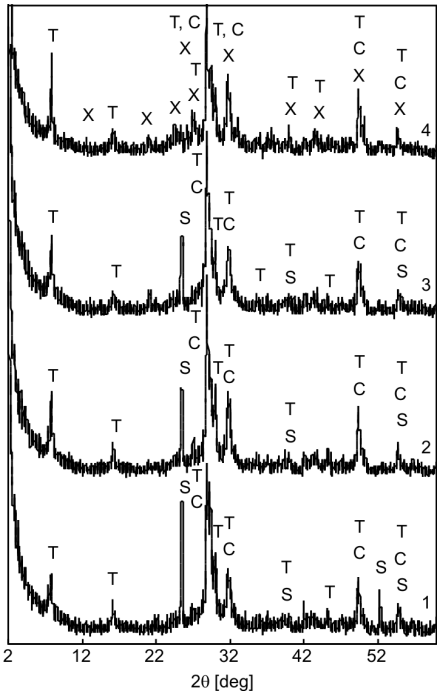

Fig. 3. X-ray diffraction patterns of the products of the syntheses when the molar ratios in the primary mixture $CaO/(SiO_2 + SO_3) = 0.83$ and $SO_3/(SiO_2 + SO_3) = 0.025$; duration (h) of hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72; C – C–S – H (I), T – 1.13 nm tobermorite, X – xonotlite, S – $CaSO_4$

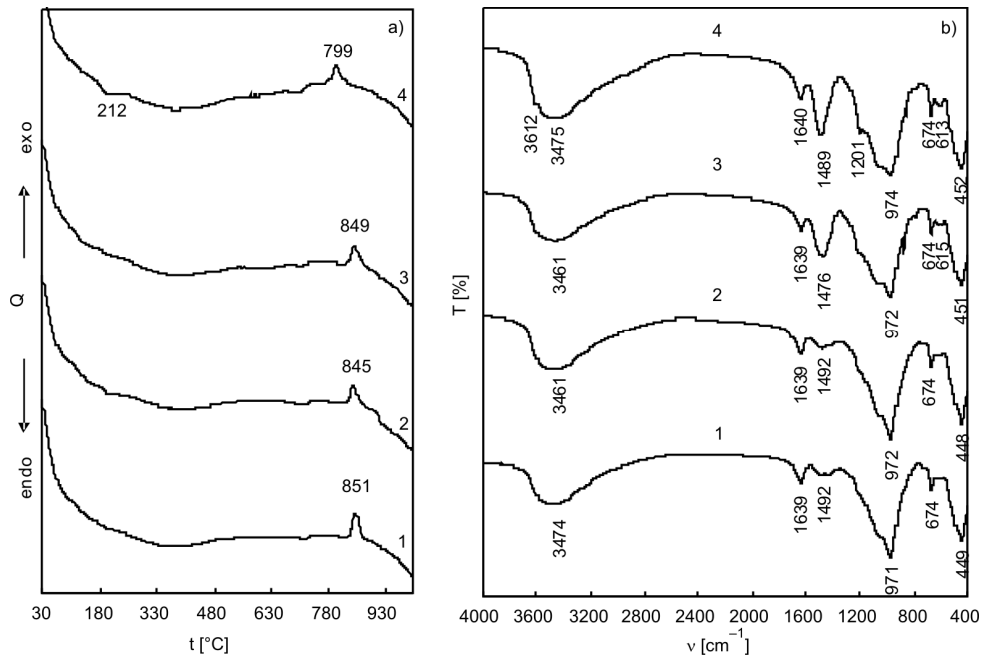

Fig. 4. DSC curves (a) and FTIR spectra (b) of the products of the syntheses when the molar ratios in the primary mixture $CaO/(SiO_2 + SO_3) = 0.83$ and $SO_3/(SiO_2 + SO_3) = 0.025$; durations of the hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72

Upon extending the synthesis to 3 days, it was confirmed that all calcium sulfate reacted and a larger amount of 1.13 nm tobermorite was formed. In this case, the basic reflections of xonotlite (*d* spacing – 0.703, 0.423, 0.341, 0.329, 0.308, 0.281, 0.224, 0.207, 0.184, 0.167 nm) were identified in the X-ray diffraction pattern (Fig. 3, curve 4). These data are confirmed by the results of DSC analysis, because the DSC curve shows the endothermic effect at 212 °C, which is typical of tobermorite, and the exothermic effect at 799 °C – C–S–H (I) (Fig. 4a, curve 4). When C–S–H (I) recrystallizes into wollastonite, sulfate ions react as flux (alloying additive), because the exothermic peak, characteristic of formation of wollastonite, significantly shifts to lower temperatures. The FTIR spectrum exhibits absorption bands characteristic of xonotlite at 3612, 1201 and 613 cm^{-1} (Fig. 4b, curve 4).

One may assume that curing the mixture of CaO, amorphous SiO_2 and $CaSO_4$ at 200 °C under saturated steam pressure, leads to formation of tobermorite in the following sequence:

$$5Ca(OH)_2 + 6SiO_2 \cdot nH_2O + XCaSO_4 + nH_2O \rightarrow 5Ca(OH)_2 \cdot 6SiO_2 \cdot nH_2O \cdot XCaSO_4 \cdot pH_2O + (n-p)H_2O$$

$$5Ca(OH)_2 \cdot 6SiO_2 \cdot nH_2O \cdot XCaSO_4 \cdot pH_2O(C-S-H\ (I)) \rightarrow 5Ca(OH)_2 \cdot 6SiO_2 \cdot mCaSO_4 \cdot pH_2O(\text{tobermorite}) + (X-m)CaSO_4$$

In the second stage of the synthesis, the quantity of $(X - m)$ $CaSO_4$, which participates in the recrystallization of C–S–H (I) into tobermorite, is different. The main fact is the large quantity of sulfate ions in the C–S–H (I) structure, relative to tobermorite. Also, the addition of gypsum reduces the solubility of $Ca(OH)_2$ and provides better conditions of the synthesis for the formation of low-base calcium silicate hydrates.

Thus, the crystallization process of 1.13 nm tobermorite is concerned with the stability of the intermediary compound – C–S–H (I) with substituted sulfate ions. Meanwhile, a larger amount of gypsum ($SO_3/(SiO_2 + SO_3) = 0.025$) stimulates the formation of not only 1.13 nm tobermorite but also of $CaSO_4$ and xonotlite.

During hydrothermal exposure in the medium of saturated water vapour, tobermorite (*d* spacing – 1.133, 0.547, 0.305, 0.281, 0.250, 0.228, 0.210, 0.184 nm) and semicrystalline C–S–H (I) (*d* spacing – 0.547, 0.305, 0.281, 0.184 nm) form in the mixture of CaO and amorphous SiO_2, for which C/S = 1.0, after 4 h (Fig. 5a, curve 1). Upon adding an appropriate amount of sulfate ions when $CaO/(SiO_2 + SO_3) = 1.0$ and $SO_3/(SiO_2 + SO_3) = 0.0125$, C–S–H (I) (*d* spacing – 0.306, 0.281, 0.184 nm) and tobermorite gel form, because the diffraction peak with *d* spacing 1.13 nm is not clear and more uneven is identified in the XRD curve (Fig. 5b, curve 1).

Upon extending the duration of synthesis to 8 h, xonotlite (*d* spacing – 0.703, 0.426, 0.364, 0.324, 0.307, 0.284, 0.271, 0.250, 0.225, 0.209, 0.195, 0.184 nm) starts forming in the mixtures because the stoichiometric C/S ratio corresponds to the molar ratio of the primary mixture (C/S = 1.0) (Fig. 5a, curve 2). Further synthesis shows

that the amount of this compound in the products of synthesis increases, and after 72 h of isothermal curing it remains the only one in the pure mixtures (Fig. 5a, curve 4).

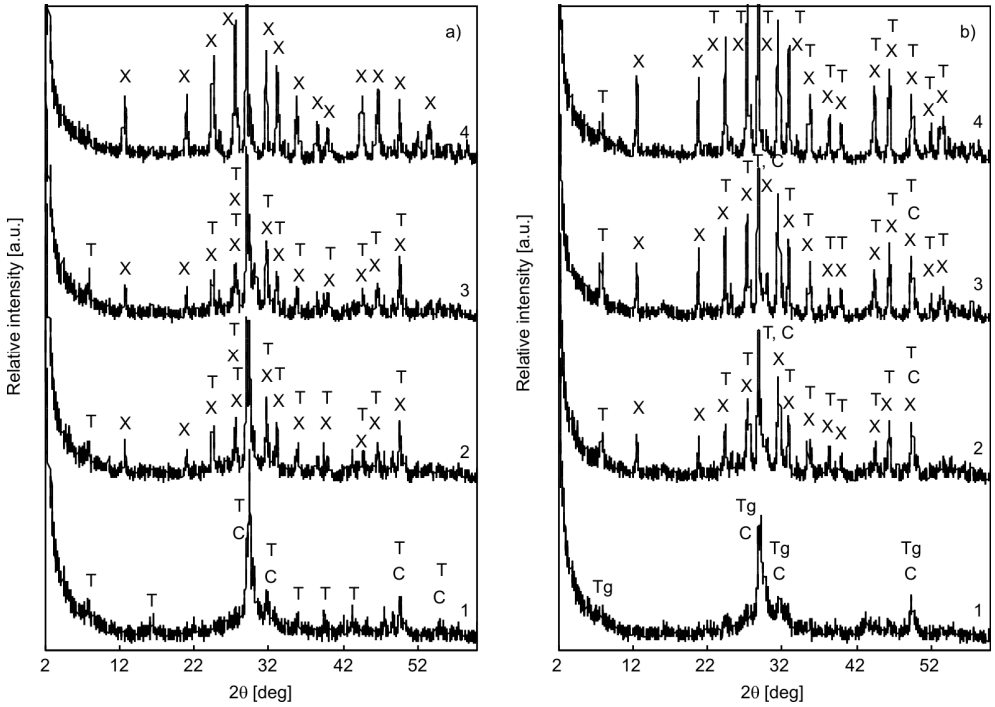

Fig. 5. X-ray diffraction patterns of the products of the syntheses when the molar ratios in the primary mixture $CaO/SiO_2 = 1.0$ (a) and $CaO/(SiO_2 + SO_3) = 1.0$, $SO_3/(SiO_2 + SO_3) = 0.0125$ (b); durations (h) of hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72; C – C–S – H (I), Tg – tobermorite gel, T – 1.13 nm tobermorite, X – xonotlite

When the mixture contains sulfate ions, the transformation of intermediate compounds into xonotlite becomes more difficult. Even after 8, 16 and 72 h, apart from the main product, xonotlite, also 1.13 nm tobermorite and/or C–S–H (I) synthesize (Fig. 5b, curves 2–4). Upon addition of a larger amounts of gypsum to the mixture ($SO_3/(SiO_2 + SO_3) = 0.025$), a slow regrouping of intermediate compounds to xonotlite was noticed. After 4 h of hydrothermal treatment only C–S–H (I) (*d* spacing – 0,308, 0,284, 0,184 nm) forms (Fig. 6, curve 1). This is additionally confirmed by the FTIR analysis because the identified absorption bands at 3450, 1646, 1484, 973, 671, 454 cm^{-1} are characteristic of calcium silicate hydrate (Fig. 7b, curve 1). DSC analysis shows that C–S–H (I) transforms into wollastonite, which is characteristic of the exothermic effect at 840 °C (Fig. 7a, curve 1). When extending the synthesis up to 8 h, as expected, C–S–H (I) starts transforming into 1.13 nm tobermorite (*d* spacing – 1.136, 0.547, 0.365, 0.324, 0.308, 0.282, 0.272, 0.203, 0.195, 0.184 nm) and xonotlite (*d* spacing – 0.705, 0.427, 0.365, 0.324, 0.308, 0.282, 0.272, 0.203, 0.195, 0.184 nm). Calcium sulfate also forms in the products (*d* spacing – 0.350, 0.234 nm) (Fig. 6, curve 2).

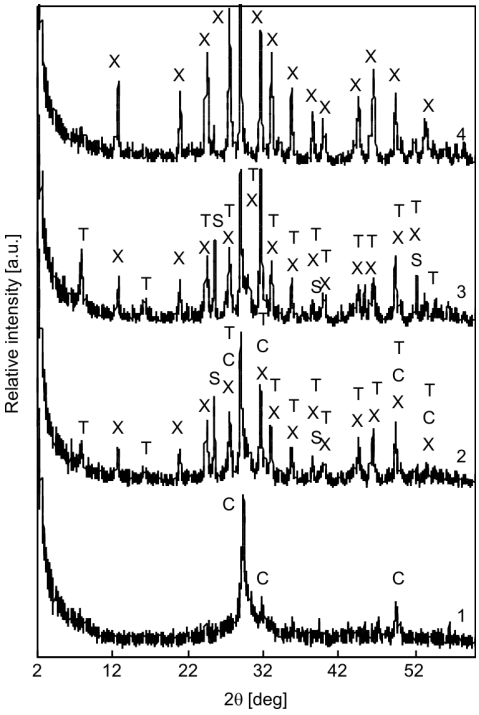

Fig. 6. X-ray diffraction patterns of the products of the syntheses when the in molar ratios in the primary mixture $CaO/(SiO_2 + SO_3) = 1.0$ and $SO_3/(SiO_2 + SO_3) = 0.025$; durations (h) of hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72; C – C–S – H (I), T – 1.13 nm tobermorite, X – xonotlite, S – $CaSO_4$

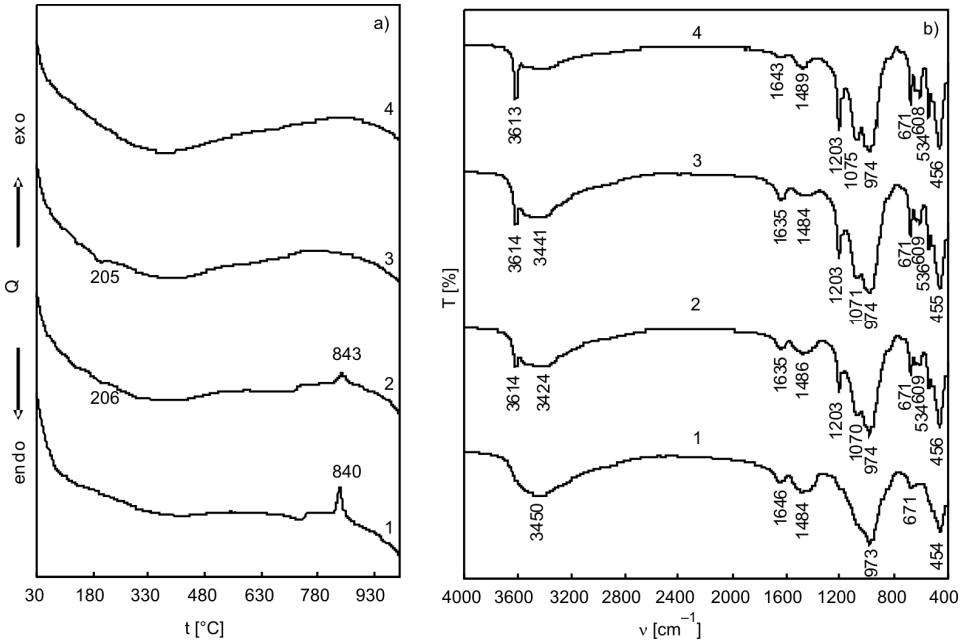

Fig. 7. DSC curves (a) and FTIR spectra (b) of the products of the syntheses when the molar ratios in the primary mixture $CaO/(SiO_2 + SO_3) = 1.0$ and $SO_3/(SiO_2 + SO_3) = 0.025$; durations (h) of hydrothermal syntheses at 200 °C: 1 – 4, 2 – 8, 3 – 16, 4 – 72

At the beginning of the synthesis all calcium sulfate penetrates into the crystal structure of semi-crystalline calcium silicate hydrates. Later on, these compounds re-crystallize into calcium silicate hydrates of more ordered structure. During this process the part of sulfate ions extrudes into solution which react with Ca^{2+} ions and form $CaSO_4$. The clear absorption band at ca. 3614 cm^{-1} testifies the crystallisation of xonotlite in the course of synthesis (Fig. 7b, curve 2). This narrow absorption band is obtained due to a clear OH position in the structure of crystal lattice as well as the shortage of hydrogen bonds.

Upon increasing the duration of crystallisation of calcium silicate hydrates (16 h), C–S–H (I) already regroups into 1.13 nm tobermorite and xonotlite. Besides, the amount of these compounds grows because much more intensive diffraction peaks (*d* spacing – 1.13 and 0.705 nm) are identified (Fig. 6, curve 3). The results of FT-IR analysis show increased intensities of absorption bands typical of these compounds (Fig. 7, b). The endothermic effect identified at a temperature of 205 °C, in the DSC curve proves the formation of 1.13 nm tobermorite and testifies to the fact that C–S–H (I) fully regroups into compounds with a higher degree of crystallinity, because exothermic effects typical of C–S–H (I) disappear in the temperature range 830–850 °C (Fig. 7a). After 72 h of isothermal curing, the only product that forms is xonotlite. These data were confirmed by the results of XRD, DSC and FTIR analyses (Figs. 6, 7).

Thus, in $CaO–SiO_2·nH_2O–CaSO_4–H_2O$ system with the C/S molar ratio equal to 1.0, at 200 °C under saturated steam pressure, sulfate substitution retards crystallization of C–S–H (I) and tobermorite. For this reason, the transformation of intermediate compounds into xonotlite is more difficult as in a pure system. It is possible to assume that in the structure of calcium silicate hydrate, sulfate ions can be bound in such a way that S^{6+} always replaces ($Si^{4+} + 2H^+$) grou

4. Conclusions

Our results show that sulfate ions can be used to improve the synthesis of 1.13 nm tobermorite in the $CaO–SiO_2·nH_2O–H_2O$ system with C/S = 0.83: after 72 h of hydrothermal treatment this compound remains stable, i.e. it does not transform into xonotlite, unlike a pure mixture. However, a larger amount of gypsum ($SO_3/(SiO_2 + SO_3)$ = 0.025) stimulates the formation not only of 1.13 nm tobermorite but also of $CaSO_4$ and xonotlite.

In the $CaO–SiO_2·nH_2O–H_2O$ system with C/S = 1.0 at 200 °C, a small amount of sulfate ions prolongs the lifetime of intermediate compounds – 1.13 nm tobermorite and C–S–H (I). The transformation of intermediate compounds becomes increasingly more difficult as the number of sulfate ions increases: during the initial stage of synthesis, calcium sulfate penetrates into the crystal structure of semi-crystalline calcium silicate hydrates. In the later synthesis stages, these compounds re-crystallize into calcium silicate hydrates of more ordered structure. Some of the sulfate ions extrude into

solution during this re-crystallization process, thereby causing a reaction with Ca^{2+} ions which ultimately results in the formation of $CaSO_4$.

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