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The influence of γ-Al_2O_3 and Na_2O on the formation of calcium silicate hydrates in the CaO–quartz–H_2O system

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The influence of γ-Al_2O_3 and Na_2O additives on the formation and sequence of calcium silicate hydrates in the CaO–quartz–H_2O system with CaO/SiO_2 (C/S) molar ratio equal to 0.66 was determined. The synthesis was carried out in unstirred suspensions. The molar ratios of the primary mixtures were $CaO/(SiO_2 + Al_2O_3) = 0.66$ and $Al_2O_3/(SiO_2 + Al_2O_3) = 0$ or 0.025. The amount of NaOH, corresponding to 5% of Na_2O in the mass of dry material, was added in the form of solution. Due to the low solubility rate of quartz in the CaO–quartz–H_2O system with C/S = 0.66 in the temperature range 150–200 °C, low-base calcium silicate hydrates (Z-phase, gyrolite, pectolite, and others) do not form even after 72 hours of hydrothermal curing. It has been proved that γ-Al_2O_3 and Na_2O additives change the reaction mechanisms and composition of intermediate (final) products. In mixtures with Na_2O, gyrolite starts to form already at 175 °C. It should be noted that in the temperature range 175–200 °C the final products are gyrolite and pectolite, and the intermediate compounds are C–S–H(I) and Z-phase. The formation of low-base calcium silicate hydrates in the CaO–quartz–Na_2O–H_2O system is slowed down when Al_2O_3 is added because Al^{3+} ions stimulate the formation of tobermorite and prevent the formation of pectolite and Z-phase.

Key words: *gyrolite; Z-phase; pectolite; tobermorite; calcium silicate hydrate*

1. Introduction

Conditions for the formation and stability of various calcium silicate hydrates in the CaO–SiO_2–H_2O (C–S–H) system have been extensively studied. C–S–Hs are a class of poorly defined calcium silicate hydrates with CaO/SiO_2 (C/S) ratios ranging from 0.44 to 3 and crystallographic structures from amorphous to highly crystalline [1–10]. As a rule, the amorphous compounds are formed during hydration of portland cement [11–13] and the crystalline ones in hydrothermal conditions [1, 4, 6]. The synthesis, properties, and structure of compounds with the molar ratio C/S from 0.8 to 1.0 (1.13 nm tobermorite, xonotlite) have been analysed in detail [1, 4–10].

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Recently, interest in low-base calcium silicate hydrates (gyrolite, Z-phase, truscottite, reyerite) has increased because the application possibilities have been found [14–16]. Meanwhile, the data presented in references about the properties of low-base compounds (C/S = 0.5–0.8) and their formation in hydrothermal conditions are not extensive and often controversial [17–21].

At the molar ratios of C/S = 0.50 and 0.66 in the system $CaO–SiO_2–H_2O$, the most stable phases under hydrothermal conditions in the temperature range 200–300 °C are truscottite and gyrolite. The phase composition of the hydrates in the given system depends on the C/S ratio chosen, the character and properties of the silicon oxide employed, as well as on the temperature and duration of the hydrothermal process. Gyrolite can be synthesized from CaO and various forms of SiO_2 with the molar ratio of C/S = 0.66 in aqueous suspension at temperatures near 200 °C. Kalousek and Nelson [22], and also Števula and Petrovič [23] have found that gyrolite could likewise be prepared by reacting dicalcium silicate ($2CaO \cdot SiO_2$) with SiO_2 in an aqueous suspension under hydrothermal conditions. Števula et al. reported that natural and synthetic gyrolite behaved analogously in the temperature range 200–300 °C under hydrothermal conditions. At 200 °C and under the pressure of saturated water vapour, gyrolite and laumonite can coexist in natural specimens owing to similar C/S ratios. Above this temperature, both natural and synthetic gyrolite decompose, forming stable phases such as truscottite and xonotlite. The stable phase association of truscottite + xonotlite + laumonite exists in the temperature range 250–300 °C [18].

Okada et al. [25], using lime and amorphous silica as the starting materials, hydrothermally prepared gyrolite with the C/S molar ratio of 0.66 and 0.50 at 200 °C for 0.5–128 h. The initially formed C–S–H consisted mainly of long chains of silicate anions. For C/S = 0.66, the chain that formed was broken, and C–S–H changed into gyrolite and xonotlite. For C/S = 0.50, only gyrolite was formed from a long chain of silicate anions. It is thought that the differences in the C–S–H structures, which were formed in the initial stage, greatly influenced the final products. In addition, for C/S = 0.50, the Z-phase was also formed as a precursor of gyrolite and its silicate anion structure was similar to that of the gyrolite [24]. Some specimens of gyrolite probably also contained small amounts of the Z-phase as impurity intergrowths [2]. The Z-phase was obtained by Funk and Thilo [25] by autoclaving calcium silicate hydrated gel at 180 °C; as well as by Assarsson [2] by autoclaving a mixture of lime and silicic acid at 195 °C. Gard et al. [21] showed that the Z-phase can be produced by decomposing Al-substituted tobermorite and they presented results of thermal electron diffraction, and infrared studies that confirm the relationship to gyrolite.

Jauberthie et al. [19] reported that tobermorite gel formed by the hydrothermal reaction of silica and lime is transformed either into the Z-phase if the quantity of lime is less than 37% or into 1.0 nm tobermorite if the quantity of lime is between 37% and 42%. The 1.0 nm tobermorite is stable in the presence of gyrolite, whereas the Z-phase is metastable [19].

Luke [26] established that at 180 °C the initially formed amorphous calcium silicate gel transforms into well-defined crystalline phases, the stabilities of which depend primarily on the C/S ratio and hydrothermal conditions. Gyrolite ($C_2S_3H_{\sim 2}$), tobermorite ($C_5S_6H_5$), truscottite ($C_7S_{12}H_{\sim 3}$), and xonotlite (C_6S_6H) were all reported to coexist stably in aqueous solutions with silica in the silica-rich part of the CaO–SiO_2 –H_2O system [26].

Shaw et al. [20], using a synchrotron X-ray radiation source of high energy, have explored the mechanical, kinetic and energetic processes proceeding during formation of gyrolite. In the temperature range 190–240 °C in a pure calcic system it involves three stages: amorphous gel, C–S–H gel and Z-phase gyrolite [20].

Crystal lattice of natural gyrolite always contains both sodium and aluminium ions [27, 28]. There are some data in the references about the influence of Al_2O_3 and Na_2O additives on the synthesis of low base calcium silicate hydrates (in contrast to 1.13 nm tobermorite) [14, 29–32]. It should be noticed that Miyake, Iwaya, and Suzuki [14] successfully synthesized (Al + Na)-substituted gyrolite ($Ca_8Si_{11.32}Al_{0.68}Na_{0.44}O_{30}(OH)_4 \cdot 6.6H_2O$) and used it for ion exchange reactions (K^+ and Cs^+) in aqueous solutions.

However, the conditions of low-base calcium silicate hydrates formation, the dependence of compounds stability on the mixture C/S ratio, as well as on the temperature and duration of the hydrothermal process were usually studied using active forms of SiO_2: finely dispersed aerosil, silicic acid, amorphous SiO_2. On the contrary, formation of the compounds is more difficult when quartz is used, and the sequence of their formation has not been determined. Therefore, it is necessary to look for additives promoting and/or accelerating the formation of the final products in the CaO–quartz –H_2O system.

The aim of this study was to determine the formation sequence of calcium silicate hydrates and their stabilities in the CaO–quartz–H_2O system with C/S = 0.66 and to examine the influence of γ-Al_2O_3 and/or Na_2O additives.

2. Experimental

The following reagents were used as starting materials: fine-grained quartz after grinding, with iron impurities washed away by hydrochloric acid (specific surface area S_a = 1100 m²/kg by Blaine); NaOH solution (c = 1.04%); CaO produced by burning $CaCO_3$ at 1000 °C for 6 hours (S_a = 548 m²/kg); γ-Al_2O_3, obtained after heating $Al(OH)_3$ for 5 hours at 550 °C (S_a = 712 m²/kg).

The synthesis of calcium silicate hydrates was carried out in unstirred suspensions in vessels of stainless steel. The molar ratios of the primary mixtures were C/(S + A) = 0.66 and A/(S + A) = 0.025 (C – CaO, S – SiO_2, A – Al_2O_3). The amount of NaOH corresponding to 5% of Na_2O in the mass of dry materials was added in the form of solution, together with the additional necessary quantity of water; the water/solid ratio of the suspension thus produced was equal to 10.0. Hydrothermal synthesis was carried out under saturated steam pressure at temperatures of 150, 175, 200 °C; the duration of isothermal curing was 4, 8, 16, 24, 32, 48, 72, or 168 hours. The products of the synthesis were filtrated, rinsed with ethyl alcohol to prevent carbonisation, dried at 100 ± 5 °C, and sieved through an N 005 sieve.

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

Simultaneous thermal analysis (STA) – comprising differential scanning calorimetry (DSC) and thermogravimetry (TG) – was also employed for measuring the thermal stability and phase transformation of the synthesized products at a heating rate of 10 °C/min; the temperature ranged from 30 to 1000 °C in ambient atmosphere. The test was carried out with a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles used were made of Pt–Rh.

Scanning electron microscopy (SEM) (Oxford ISIS Leo 440 i, UK), coupled with energy dispersive X-ray spectrometry (EDS) of the samples, was performed using the accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation and a 200 s accumulation time for EDS analysis.

IR spectra were carried out with Perkin Elmer FT-IR system spectrum X spectrometer. Specimens were prepared by mixing 1 mg of the sample with 200 mg of KBr. Spectral analysis was performed in the range 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.

3. Results and discussion

In a pure CaO–quartz–H_2O mixture after 24 hours of isothermal curing at 150 °C, the compounds with higher basicity – dicalcium silicate hydrates – α-C_2S hydrate and calcium silicate hydrates of unspecified composition with C/S > 1.5 (C–S–H(II)) were formed due to the fact that quartz dissolved slower than $Ca(OH)_2$ and the solution contained a significant excess of Ca^{2+} ions (Fig. 1, curve 1; Table 1). When hydrothermal synthesis was extended up to 48 hours, almost all of the $Ca(OH)_2$ reacted and the intensity of the basic reflections of quartz in the XRD pattern slightly decreased. This variation can be assigned to the dissolution of a significant amount of quartz, which stimulates the decomposition of C–S–H(II) and α-C_2S hydrate, the latter only remaining in traces. Consequently, calcium silicate hydrate of unspecified composition of C/S between 0.8 and 1.5 (C–S–H(I)) and a small quantity of 1.13 nm tobermorite form in the products. As was expected, when synthesis is continued (168 h) all of the α-C_2S hydrate decomposes and 1.13 nm tobermorite starts to prevail in the product (Table 1).

At the beginning of the reaction (24 h), the Al_2O_3 additive did not change the sequence of calcium silicate hydrate formation – α-C_2S hydrate, C–S–H(II), quartz, and

$Ca(OH)_2$ dominate the products (Fig. 1, curve 2; Table 1). It should be noticed that the compounds of the calcium aluminium silicate hydrate groups began to form when synthesis was prolonged to 48 h.

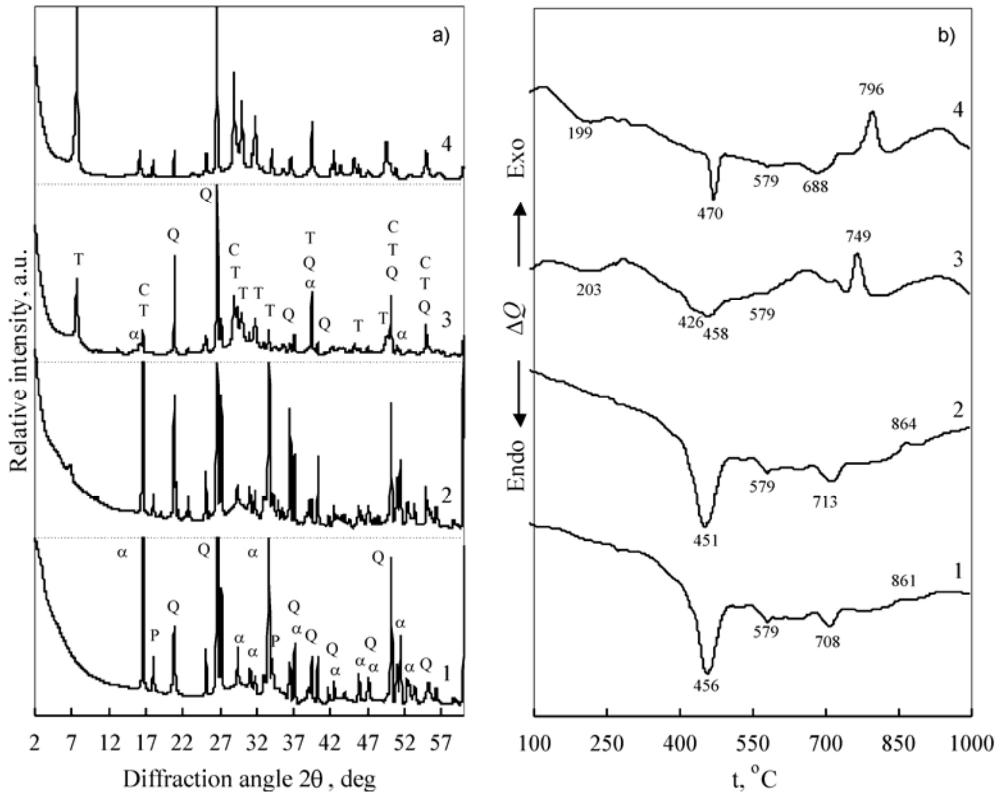

Fig. 1. X-ray diffraction patterns (a) and DSC curves (b) of the products of synthesis: 1 – pure CaO–quartz–H_2O mixture; 2 – with Al_2O_3 additive; 3 – with Na_2O additive; 4 – with (Al_2O_3 + Na_2O) additive; indices: α – α-C_2S hydrate, P – portlandite, Q – quartz, C – C–S–H(I), T – 1.13 nm tobermorite; the duration of hydrothermal synthesis at 150 °C was 24 h

Many compounds form the group of calcium aluminium silicate hydrates or hydrogarnets, with almost the same interplanar distances *d*, and as a result their peaks overlap. The basic reflection intensities of the mentioned compounds in the X-ray diffraction patterns are rather small, as only 2.6% of Al_2O_3 was added to the initial mixture, and that is why it is very difficult to assign products to particular compounds. For this reason, these compounds will be named as calcium aluminium silicate hydrates (CASH), where the number of SiO_2 moles varies from 0 to 3.

It should be underlined that Al_2O_3 prolongs the existence of dibasic calcium silicate hydrates, and Al-substituted tobermorite forms only after 168 h of hydrothermal treatment. Furthermore, during this period CASH fully decompose.

Table 1. Stability of calcium silicate hydrates at 150 °C when the initial mixture molar ratio C/S = 0.66*

Initial mixture	Duration of curing (h)	P	Q	α	C(II)	C(I)	C	T
CaO–quartz–H_2O	24	●	●	●	●			
	48	●	●	●		●		●
	168		●			●		●
CaO–quartz–Al_2O_3–H_2O	24	●	●	●	●			
	48	●	●	●	●		●	
	168		●	●		●		●
CaO–quartz–Na_2O–H_2O	4	●	●	●				
	16	●	●	●		●		
	24	●	●	●		●		●
	72					●		●
CaO–quartz–Al_2O_3–Na_2O–H_2O	4	●	●				●	●
	16	●	●			●	●	●
	24	●	●			●		●
	72		●			●		●

*P – portlandite, Q – quartz, α – α-CS_2 hydrate, C(I) – C–S–H(I), C(II) – C–S–H(II), C – Calcium aluminum silicate hydrates, T – 1.13 nm tobermorite.

Na_2O intensified the hydrothermal reactions in the CaO–quartz–H_2O system. The main reason for this phenomenon was the presence of Na^+ ions in the solution accelerating the solubility rate of quartz by eroding the surface of particles and increasing the concentration of SiO_4^{4-} ions in the solution. The traces of α-C_2S hydrate are formed after the first 4 hours of synthesis, although large quantities of $Ca(OH)_2$ and unreacted quartz remain. Therefore, already after 16 h of isothermal curing C–S–H(I) begins to form, because the amount of unreacted quartz decreases. It should be stressed that dibasic calcium silicate hydrates are less stable than in the pure mixtures: after 16 h of synthesis they start to decompose, and after 24 h they almost fully transform into C–S–H(I) and 1.13 nm tobermorite (Fig. 1, curve 3). Quartz did not react completely even in 72 hours of synthesis, however, neither in pure mixtures nor in mixtures with the Na_2O additive (Table 1). Due to a low quartz solubility rate, the stoichiometric C/S ratio (0.66) of the primary mixture was not reached and both C–S–H(I) and 1.13 nm tobermorite dominated in the products.

In the CaO–Al_2O_3–SiO_2–H_2O mixture, Na^+ ions increase the solubility rate of quartz, too. On the other hand, Al^{3+} ions stimulated the formation of tobermorite and CASH: in the products they were identified already after 4 hours of isothermal curing. CASH began to decompose after 16 h of synthesis and tobermorite, together with C–S–H(I) and quartz, remained during the entire hydrothermal treatment (Table 1).

Thus, at 150 °C both Na_2O and complex (Al_2O_3 + Na_2O) additives accelerated the reactions by affecting the decomposition of dibasic calcium silicate hydrates and the formation of compounds of lower basicity. This temperature was still too low for the synthesis of low-base calcium silicate hydrates (Z-phase, gyrolite, pectolite), however, as even after 168 h of isothermal curing a large quantity of quartz remained in the products.

In order to increase the reaction rate and avoid the formation of dicalcium silicate hydrates, hydrothermal synthesis was carried out at higher temperatures. In pure mixtures at 175 °C, after 16 hours of synthesis α-C_2S hydrate, C–S–H(II), $Ca(OH)_2$, and traces of 1.13 nm tobermorite form (Fig. 2, curve 1; Table 2).

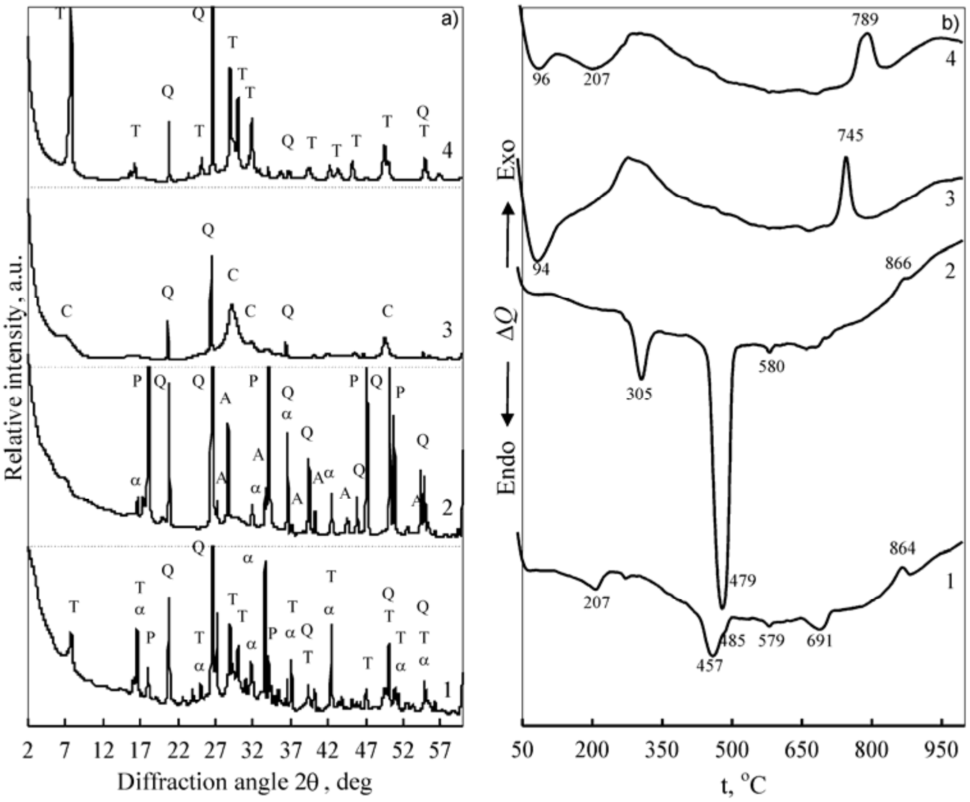

Fig. 2. X-ray diffraction patterns (a) and DSC curves (b) of the products of synthesis: 1 – pure CaO–quartz–H_2O mixture; 2 – with Al_2O_3 additive; 3 – with Na_2O additive; 4 – with (Al_2O_3 + Na_2O) additive; indices: α – α-C_2S hydrate, P – portlandite, Q – quartz, C – C–S–H(I), T – 1.13 nm tobermorite; the duration of hydrothermal synthesis at 175 °C was 16 h

Already in 1974, Taylor [33] noticed that at temperatures above 150 °C tobermorite is thermodynamically unstable in mixtures with C/S > 0.8, and that this compound tends to turn into xonotlite. This finding is confirmed by our experimental results: at sufficiently long hydrothermal curing (48 hours), when dibasic calcium silicate hydrates fully decompose, tobermorite partly transforms into xonotlite and not gyrolite, because even in the mixture reacting at 175 °C the C/S ratio is higher than 0.66 due to the low quartz solubility rate. It should be noticed that both 1.13 nm tobermorite and xonotlite dominate in the products even after 72 hours of isothermal curing (Table 2).

Table 2. Stability of calcium silicate hydrates at 175 °C when the initial mixture molar ratio C/S = 0.66*

Initial mixture	Duration of curing (h)	P	Q	α	C(II)	C(I)	C	T	X	P	G	Z
CaO–quartz–H_2O	16, 24, 32	●	●	●		●		●				
	48, 72		●			●		●	●			
CaO–quartz–Al_2O_3–H_2O	16	●	●	●	●		●					
	24	●	●	●	●	●	●	●				
	32		●	●	●	●	●	●				
	48		●			●		●				
	72		●					●	●			
CaO–quartz–Na_2O–H_2O	4, 8, 16, 24, 32		●			●						
	72		●			●		●				
	168		●					●		●	●	●
CaO–quartz–Al_2O_3–Na_2O–H_2O	4	●	●			●	●	●				
	8, 16, 24, 32		●			●		●				
	72					●		●				
	168					●		●			●	

*P – portlandite, Q – quartz, α – α-CS_2 hydrate, C(I) – C–S–H(I), C(II) – C–S–H(II), C – calcium aluminum silicate hydrates, T – 1.13 nm tobermorite, X – xonotlite, P – pectolite, G – gyrolite, Z – Z-phase.

At 175 °C Al_2O_3 additive did not influence the formation and stability of α-C_2S hydrate, but retarded the formation of 1.13 nm tobermorite, which was identified in the products only after 24 h of synthesis; when in the pure mixture, after 16 h (Fig. 2, curves 1, 2). CASH fully decomposed after 48 h of isothermal curing and released Al^{3+} ions enter into the crystal structure of tobermorite or C–S–H(I). C–S–H(II) finished transforming into C–S–H(I), since the exothermic peak of that compound disappeared from the DSC curve.

It is well known that in mixtures with the molar ratio of C/S = 1.0, Al_2O_3 additives impede the formation of xonotlite. Our results show that the same sequence of calcium silicate hydrates form in the low basicity mixtures (C/S = 0.66), too. The most characteristic *d*-spacing of xonotlite in the XRD pattern (0.70 nm) was observed only after 72 h of synthesis at 175 °C (in the mixtures without aluminium additives after 48 h). Meanwhile, unreacted quartz remained in the products dominated by highly crystalline Al-substituted tobermorite (Table 2).

In the mixture with Na_2O, there was a substantial change in the sequence of calcium silicate hydrate formation at 175 °C: $Ca(OH)_2$ reacts completely and only a semi-crystalline C–S–H(I) is formed during the first 4 hours of synthesis. It should be emphasized that dibasic calcium silicate hydrates are not formed at this temperature or at 200 °C. This can be explained by the presence of Na^+ ions in the solution, which accelerate the solubility rate of quartz. It should be noted that the final amount of unreacted quartz (10–15%) dissolved very slowly and C–S–H(I) formed only after 8 hours of hydrothermal treatment (Fig. 2, curve 3; Table 2). At 175 °C, due to a rapid decrease of the C/S ratio to 0.7, 1.13 nm tobermorite was only the intermediary compound, because after 72 h of isothermal curing rudiments of calcium sodium silicate hydrate (pectolite) coexist. When synthesis was prolonged to 168 h, the amount of tobermorite decreased and low-base calcium silicate hydrates (pectolite, gyrolite, and Z-phase) prevail in the products (Fig. 3, curve 1).

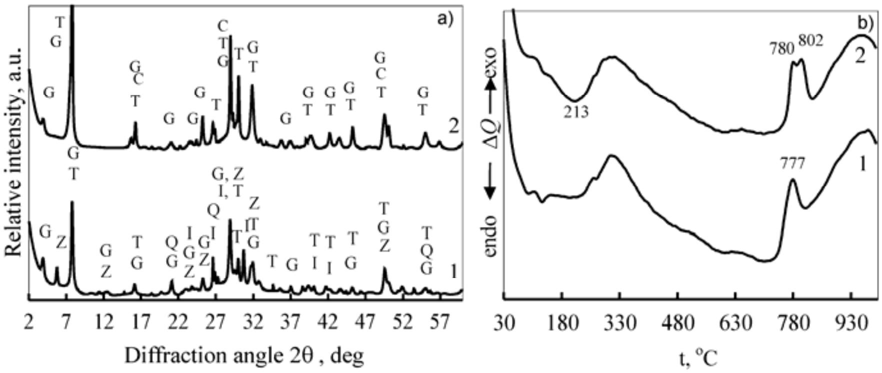

Fig. 3. X-ray diffraction patterns (a) and DSC curves (b) of the products of synthesis: 1 – with Na_2O additive; 2 – with (Al_2O_3 + Na_2O) additive; indices: Q – quartz, C – C–S–H(I), T – 1.13 nm tobermorite, I – pectolite, Z – Z-phase, G – gyrolite; the duration of hydrothermal synthesis at 175 °C was 168 h

Thus, low-base calcium silicate hydrates can be synthesized when a less active SiO_2 modification (quartz) and sodium oxide are used. Larger quantities of these compounds, however, form only after 168 hours of isothermal curing at 175 °C.

It was determined that in CaO–quartz mixtures the complex (Al_2O_3 + Na_2O) additive greatly accelerated the formation of 1.13 nm tobermorite and C–S–H(I) at 175 °C: those compounds were identified already after 4 h of synthesis (Table 2). The exothermic peak of C–S–H(I) at 813 °C became wider than in the mixtures without additives. It is presumable that they were affected by Al^{3+} and Na^+ ions, which entered the crystal structures of both tobermorite and C–S–H(I). Also, it was observed that Al^{3+} ions interfered in the crystal structures of calcium silicate hydrates significantly rather than at 150 °C, because traces of CASH were identified only at the beginning of synthesis (Table 2).

Thus, Al^{3+} and Na^+ions interfered in the crystal structures of calcium silicate hydrates and stabilized them. Almost the same quantities of 1.13 nm tobermorite and C–S–H(I) remain unchanged after 24, 48, and 72 hours of hydrothermal treatment.

After 168 h of isothermal curing, it started to transform into gyrolite (Fig. 3a, curve 2). The formation of Z-phase and pectolite was not observed, as in the mixtures with Na_2O (Fig. 3a, curve 1). The XRD data were confirmed by DSC measurements, and in the DSC curve the two exothermic peaks at 780 °C, characteristic of C–S–H(I), and at 802 °C, associated to gyrolite, are observed (Fig. 3b, curve 2). (Al + Na) -substituted tobermorite formed together with gyrolite and C–S–H(I) is stable (the intensities of the basic reflections do not change after prolonging hydrothermal treatment from 24 to 168 h). Thus, at 175 °C gyrolite was successfully synthesized when an SiO_2 modification (quartz) was used, although other calcium silicate hydrates were formed together with it, namely 1.13 nm tobermorite and C–S–H(I).

Table 3. Stability of calcium silicate hydrates at 200 °C when the initial mixture molar ratio C/S = 0.66*

Initial mixture	Duration of curing (h)	P	Q	α	C(I)	C	T	X	P	G	Z
CaO–quartz–H_2O	4, 16, 24, 32		●		●		●	●			
	48, 72, 168		●				●	●			
CaO–quartz–Al_2O_3–H_2O	4, 16	●	●	●	●	●	●				
	24		●	●	●	●	●	●			
	32		●		●		●	●			
	48, 72		●		●		●	●			
	168		●		●		●				
CaO–quartz–Na_2O–H_2O	4, 8		●		●						
	16		●		●					●	●
	24		●						●	●	●
	32, 48, 72, 168								●	●	
CaO–quartz–Al_2O_3–Na_2O–H_2O	4, 8		●		●		●				
	16, 24		●		●		●			●	
	32				●		●			●	
	48, 72, 168						●			●	

*P – portlandite, Q – quartz, α – α-CS_2 hydrate, C(I) – C–S–H(I), C – calcium aluminum silicate hydrate, T – 1.13 nm tobermorite, X – xonotlite, P – pectolite, G – gyrolite, Z – Z-phase.

It should be pointed out that in the CaO–quartz–H_2O system neither α-C_2S hydrate nor C–S–H(II) formed at 200 °C. After 4 hours of isothermal curing, xonotlite formed, together with 1.13 nm tobermorite. These compounds were stable after prolonging the duration of isothermal curing to one week (Table 3). Quartz does not dissolve even after 168 h (Fig. 4, curve 1), however, and the quantity of 1.13 nm tobermorite changes unevenly, increases and decreases. We suppose that this is related to the changing C/S ratio during synthesis.

The Al_2O_3 additive slightly changed the sequence of calcium silicate hydrate formation. Primarily, like for lower temperatures, α-C_2S hydrate and CASH form, together with traces of C–S–H(I) and 1.13 nm tobermorite. Afterwards, when dibasic calcium silicate hydrates start to decompose, the amount of tobermorite increases, and xonolite begins to form. It should be underlined that the latter is not stable in mixtures of low basicity – after 168 hours of isothermal curing almost all quartz dissolved, and the C/S ratio was approximately 0.66 and almost all of the xonolite turned into 1.13 nm tobermorite (Fig. 4, curve 2).

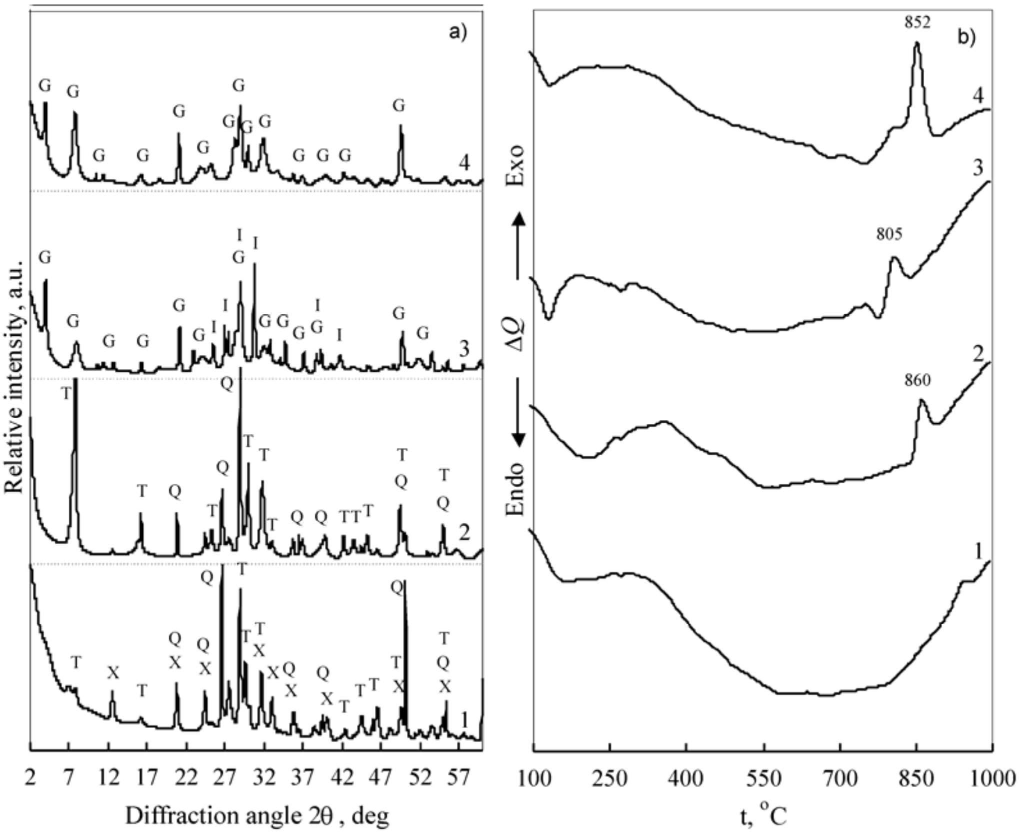

Fig. 4. X-ray diffraction patterns (a) and DSC curves (b) of the products of synthesis: 1 – pure CaO–quartz–H_2O mixture; 2 – with Al_2O_3 additive; 3 – with Na_2O additive; 4 – with (Al_2O_3 + Na_2O) additive; indices: Q – quartz, T – 1.13 nm tobermorite, X – xonotlite, I – pectolite, G – gyrolite. The duration of hydrothermal synthesis at 200 °C was 168 h

At 200 °C, Na_2O greatly affects the solubility rate of quartz, significantly accelerates the hydrothermal process, and totally changes the sequence of calcium silicate hydrate formation (Table 3). After 4 hours of synthesis, a large quantity of C–S–H(I) was formed and the larger part of the quartz reacted. After prolonged synthesis (16 hours), almost all of the quartz reacted. Therefore, it is not a coincidence that the basic peaks, characteristic of gyrolite (*d* spacing – 2.2 nm) and Z-phase (*d* spacing – 1.5 nm), start to dominate in the X-ray diffraction pattern of the reaction products. This is confirmed by DSC data: the exothermic peak at ~782 °C moves towards lower temperatures (~66 °C) and becomes wider.

It should be noted that the Z-phase was not stable in the mixtures with Na_2O, after 24 hours of hydrothermal synthesis only traces of this compound remained and already after 32 hours it finished transforming into gyrolite and pectolite. These compounds remain stable even after 168 h of isothermal curing (Fig. 4, curve 5). The accumulation of two morphologies crystals can be seen in the SEM micrographs: plate-shaped crystals characteristic of gyrolite and long, needle-shaped crystals characteristic of pectolite (Fig. 5, a).

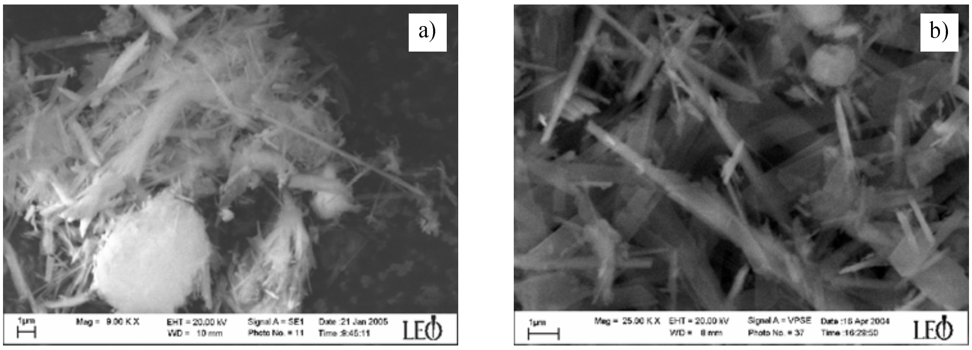

Fig. 5. SEM micrographs with Na_2O (a) and ($Al_2O_3 + Na_2O$) (b) additives; duration of isothermal curing at 200 °C was 168 h and 48 h, respectively

The formation of low-base calcium silicate hydrates in the $CaO–SiO_2–Na_2O–H_2O$ system is rather slowed down when Al_2O_3 is added, because Al^{3+} ions stimulate the formation of tobermorite and after 16 hours of isothermal synthesis only traces of gyrolite were identified. When hydrothermal synthesis is continued, gyrolite further forms but even after 168 hours of synthesis 1.13 nm tobermorite remained in the products. At 175 °C, the presence of Al_2O_3 additive prevents the formation of pectolite and Z-phase (Fig. 4, curve 4). SEM observations confirmed that 1.13 nm tobermorite and gyrolite dominate in the products (Fig. 5b).

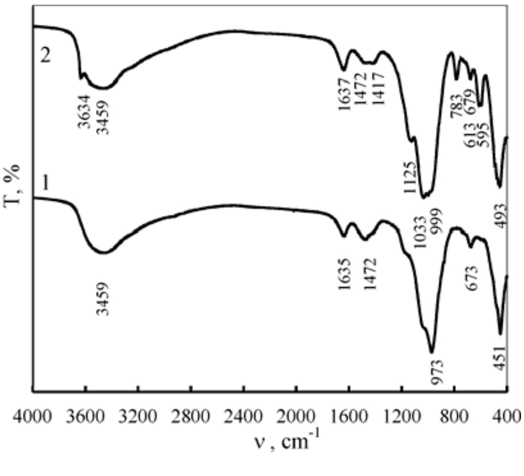

Fig. 6. IR spectra of the products of synthesis of the $CaO–quartz–Na_2O–Al_2O_3–H_2O$ system; the duration of hydrothermal synthesis at 200 °C was 16 h (1) and 72 h (2)

All the data presented above have been confirmed by IR spectroscopy, which can be used to distinguish gyrolite from the Z-phase as well as from other calcium silicate hydrates [34, 35]. IR spectroscopy data show that after 16 h of synthesis the adsorption bands characteristic of tobermorite dominate (Fig. 6, curve 1). After extending the duration of isothermal curing (24, 32, 72 h), a doublet near ~595 and ~613 cm^{-1} due to Si–O–Si bending vibrations becomes more intensive, and gyrolite has two bands in the range 679–786 cm^{-1} (Fig. 6, curve 2). A sharp peak near 3634 cm^{-1}, which is visible only in the gyrolite spectrum, is missing in the IR spectra of all other calcium silicate hydrates. This clear band (3634 cm^{-1}) proves that clearly distinguished OH positions exist in the structure of gyrolite, being connected only to Ca atoms and the groups not being influenced by hydrogen bridge links.

4. Conclusions

- In the CaO–quartz–H_2O system with C/S = 0.66 the reactions proceed very slowly and low-base calcium silicate hydrates do not form in the temperature range 150–200 °C. α-C_2S hydrate and C–S–H(II) prevail during the beginning of synthesis, gradually recrystallising into 1.13 nm tobermorite and xonotlite, which remain stable even after 168 hours of isothermal curing.
- γ-Al_2O_3 has little influence on the hydrothermal process. At the beginning of the reaction this additive prolongs the lifetime of dibasic calcium silicate hydrates, and retards the formation of 1.13 nm tobermorite and its transformation into xonotlite.
- Na_2O increases the solubility rate of quartz and greatly affects the sequence of calcium silicate hydrate formation. In the temperature range 175–200 °C, the intermediate compounds are C–S–H(I) and the Z-phase, and the final products are gyrolite and pectolite.
- The complex (Al_2O_3 + Na_2O) additive stimulates the decomposition of α-C_2S hydrate, but prevents the formation of the Z-phase and pectolite. Gyrolite forms analogously as in the mixture with Na_2O, although it always coexists with 1.13 nm tobermorite.

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