

Formation of gyrolite in the CaO–quartz–Na₂O–H₂O system

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Optimizing the duration and/or the temperature of hydrothermal synthesis of gyrolite has been investigated by adding NaOH solution into an initial mixture of CaO–quartz–H₂O. The molar ratio of the primary mixture was C/S = 0.66 (C – CaO; S – SiO₂). An amount of NaOH, corresponding to 5 % Na₂O from the mass of dry materials, added in the form of solution and additional water was used so that the water/solid ratio of the suspension was equal to 10.0. Hydrothermal synthesis of the unstirred suspension was carried out in saturated steam at 150, 175, 200 °C. The duration of isothermal curing was 4, 8, 16, 24, 32, 48, 72 and 168 h. The temperature of 150 °C is too low for the synthesis of gyrolite; the stoichiometric ratio C/S = 0.66 is not reached even after 168 h of synthesis neither in pure mixtures nor in mixtures with addition of Na₂O. Na⁺ ions significantly influence the formation of gyrolite from the CaO–quartz mixtures in the temperature range from 175 °C to 200 °C. Gyrolite is formed at 175 °C after 168 h and at 200 °C after 16 h of isothermal curing. On the contrary, in pure mixtures it does not form even after 72 h at 200 °C. Na⁺ ions also change the compositions of intermediate and final products of the synthesis. In mixtures with 5% Na₂O, intermediate compounds are C–S–H(I) and Z-phase, and the final products are gyrolite and pectolite. Meanwhile, in mixtures without this additive, the main intermediate compounds are α -C₂S hydrate and C–S–H(II), and the main products are 1.13 nm tobermorite and xonotlite.

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

1. Introduction

Gyrolite (Ca₂Si₃O₇(OH)₂·xH₂O), calcium silicate hydrate (C–S–H), rarely occurs as a natural mineral in association with zeolites and often forms nodular aggregates. These aggregates can appear glassy, dull or even fibrous [1]. Hydrothermal synthesis of gyrolite is a long and complex process. Flint et al. [2], who first synthesized gyrolite, reported that the product is formed from a mixture of CaO and SiO₂ after 6–42 days of hydrothermal synthesis at 150–350 °C when the molar ratio CaO/SiO₂

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(C/S) of the starting materials changes from 0.5 to 0.66. This data was later confirmed by the results of thermodynamical calculations [3].

It is known that various ions (Na^+ , K^+ , Cs^+ , Cu^{2+} , Fe^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Mg^{2+}) in the crystal lattice of calcium silicate hydrates (mainly 1.13 nm tobermorite, 1.13 nm-substituted tobermorites and xonotlite) can substitute some of Ca^{2+} or Si^{4+} ions in the structure under hydrothermal reaction, altering their physicochemical behaviour. The effectiveness of each additive may change depending on the properties of the raw materials, parameters of the hydrothermal reactions and other factors. Numerous authors describe the influence of alkali metals [4–6], aluminum [7–10] and other elements with additives [11, 12] on the synthesis and properties of calcium silicate hydrates, however little is known about the cavities into which these ions substitute.

Basicity of synthesized calcium silicate hydrates described in terms of the C/S molar ratio is influenced more by alkaline additives than by changes in temperature. Depending on the concentration of Na^+ ions, the ratio of water/solid materials and the initial composition of the mixture, duration of the hydrothermal synthesis may be significantly reduced [9]. Blakeman et al. [6] found that at a constant C/S molar ratio of 0.83 and a varying quantity of NaOH in the primary mixtures, various compounds are formed (C–S–H(I), 1.13 nm tobermorite, pectolite, xonotlite).

Nocun-Wczelik [9, 10] investigated the influence of additives containing sodium and aluminum oxides on the composition and properties of calcium silicate hydrates. The author found that during hydrothermal treatment of CaO- and SiO_2 -bearing components, Na^+ ions accelerate the formation of poorly crystallized calcium silicate hydrates but further transformation of this intermediate product into more-ordered, well-developed crystalline forms can be disturbed at some admixture content. Xonotlite is the final product of the synthesis when the C/S molar ratio of the primary mixture is equal to 1.0. However, if over 20% of Na_2O is added into the mixture, all of the intermediate products, which are ordered phases of calcium silicate hydrates transform into tobermorite. Meanwhile, the formation of gyrolite or Z-phase in mixtures with a lower C/S ratios (0.67 or less) is faster in pure suspensions and, in addition, a C–S–H(I) residue is present when there is a Na_2O admixture of 5–10%.

It is often stated that the crystal lattice of natural gyrolite always contains both sodium and aluminium ions [13]. This presumption has been confirmed by many tests of Merlino who reported that the most likely composition of natural gyrolite is $\text{NaCa}_{16}\text{Si}_{23}\text{Al}_{60}(\text{OH})_8 \cdot 14\text{H}_2\text{O}$. However, Sukheswala et al. [14] reported that natural gyrolite from both the Deccan Traps near Bombay, India, and the Dean quarry apparently contain no Al. According to Seager [15], gyrolite was formed later than calcite in which it is embedded, or perhaps simultaneously with late stages of calcite formation. Hydrothermal solutions responsible for the formation of gyrolite may have become depleted of Al by earlier deposition of prehnite, providing a possible explanation for the unusually low Al content in gyrolite both in the Deccan Traps and at a Dean quarry [16].

Many authors investigated crystal structure of gyrolite [13, 17, 18]. They noticed that the interlayer sheets with a thickness of about 0.3 nm in gyrolite are available for

the intercalation of a new guest by controlling the charge in the host. For example, Na⁺ ions can be incorporated into the interlayer sheets by replacing Si⁴⁺ with Al³⁺ ions in the complex layers in order to maintain charge neutrality. Intercalated Na⁺ ions were expected to be exchangeable for univalent cations in aqueous solution [8].

Shaw [19] reported that the rate for gyrolite formation in a sodium-bearing system is significantly higher than reactions in a pure calcic system at the same temperature. The presence of sodium in this system in the form of a 1 M NaOH solution changes the mechanism of gyrolite formation. There is no intermediate formation of Z-phase and a mixture of gyrolite and pectolite forms directly from C–S–H gel [19].

Miyake, Iwaya and Suzuki [8] successfully synthesized Al-substituted gyrolite (Ca₈Si_{11.32}Al_{0.68}Na_{0.44}O₃₀(OH)₄·6.6H₂O) and used it for the exchange reactions of ions (K⁺ and Cs⁺) in aqueous solutions. Since the specimen has a smaller amount of Na⁺ ions than of substituted Al³⁺ ions, it was supposed that Ca²⁺ ions make up for the deficiency in order to keep charge neutrality. Al-substituted gyrolites retained their crystal structure and showed the same behaviour on heating and the same lamellar morphologies as the original one. In addition, basal spacing of gyrolite, d-spacing 2.2 nm, was not altered after the uptake of K⁺ and Cs⁺ ions. Moreover, it is easier to intercalate K⁺ ions than Cs⁺ ions into the crystal lattice of this compound. However, the authors noticed that Cs⁺ ions are better absorbed by Al-substituted tobermorite [20, 21]. Al-substituted gyrolite may be used to eliminate heavy metal ions and remove them from wastewaters [22, 23] and it is known for its selectivity to DNA [24].

However, all of these tests were performed with SiO₂ component using its active forms such as amorphous SiO₂, finely dispersed aerosol and silicic acid. There is little data about the effect of a less active form of SiO₂ on the synthesis of gyrolite and the sequence of the formed new compounds and the influence of additives on these processes. Our results show that in the CaO–quartz–H₂O mixtures neither Z-phase, nor gyrolite forms, even during 72 h of hydrothermal curing due to low quartz solubility rate at temperature range from 150 °C to 200 °C [25, 26]. The results published elsewhere [9, 10, 19] demonstrate that Na⁺ ions in many cases stimulate the formation of calcium silicate hydrates, especially when the starting materials are not very active. It is likely that they will have a positive influence the gyrolite formation processes as well. The purpose of this paper was to examine the possibility of reducing the duration and/or temperature of hydrothermal synthesis of gyrolite by adding NaOH solution into the initial CaO–quartz–H₂O mixture.

2. Experimental

The following reagents were used as starting materials: fine-grained quartz (specific surface area 1100 m²/kg by Blaine), after grinding washed away from iron impurities by hydrochloric acid; NaOH solution (1.04 %); calcium oxide (specific surface area 548 m²/kg by Blaine) which had been produced by burning calcium carbonate at 1000 °C for 6 h.

The synthesis of calcium silicate hydrates has been carried out in unstirred suspensions in vessels of stainless steel. The molar ratio C/S of the primary mixture was 0.66. The amount of NaOH corresponding to 5% of Na₂O from the mass of dry materials was added in the form of solution. The suspension was diluted with water so that the water/solid ratio was equal to 10.0. Hydrothermal synthesis has been carried out under the saturated steam pressure at 150, 175, 200 °C; the duration of isothermal curing was 4, 8, 16, 24, 32, 48, 72 or 168 h. The products of the synthesis were filtered, rinsed with ethyl alcohol to prevent carbonization of the material, dried at 100 ± 5 °C and sieved through the sieve No. 005.

The X-ray powder diffraction data were collected with a DRON-6 powder X-ray diffractometer with the Bragg–Brentano geometry using Ni-filtered CuK_α radiation and graphite monochromator, operating at a voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2–60° (2θ) in steps of 2θ = 0.02°. For diffraction profile refinement under the pseudoVoigt function and for a description of the diffractive background under the 3rd degree Tchebyshev polynomial, we used the X-fit computer program [27].

Thermal analyzer DuPont 990 (USA) with computerized control and data recording was applied for differential thermal analysis (DTA) and for differential scanning calorimetry (DSC) studies. For DTA, the heating was carried out in air, the rate of temperature increase was 10 °C/min, the temperature range from 100 up to 1000 °C. The ceramic sample handlers and Al₂O₃, as an inert material, were used. The DSC parameters were: the rate of temperature increase was 10 °C/min, temperature interval was 20–550 °C, and empty aluminum capsule as an inert material was used.

The specific surface area of the raw materials was determined by the Blaine's method. FTIR spectra have been obtained with a Perkin Elmer FT-IR system Spectrum X spectrometer. The specimens were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range 4000–400 cm⁻¹ with the spectral resolution of 1 cm⁻¹.

3. Results and discussion

Na₂O additive positively affects the hydrothermal reactions in the CaO–quartz–H₂O system. After first 4 h of synthesis at 150 °C, traces of α-C₂S hydrate are already formed in the products and a large quantity of Ca(OH)₂ and quartz remain unreacted (Fig. 1, curve 1). Due to the fact that quartz dissolves slower than Ca(OH)₂ and the solution contains a significant excess of Ca²⁺ ions, the compounds of a higher basicity – dicalcium silicate hydrates – are formed. These results were confirmed by DTA and DSC analysis data. The endothermic effect, which is characteristic of the α-C₂S hydrate, was possible to identify only by the DSC method (Fig. 2, curve 1, endothermic peak at *t* = 505 °C). This peak is covered by a wide and more intensive Ca(OH)₂ dehydration peak in the DTA curve (Fig. 1b, curve 1, endothermic peak at *t* = 503 °C).

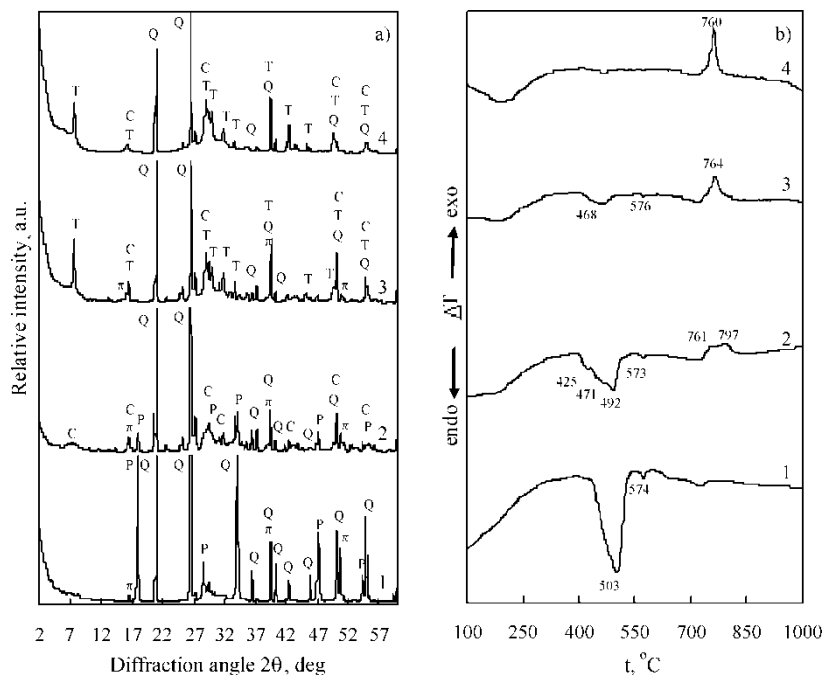


Fig. 1. X-ray diffraction patterns (a) and DTA curves (b) of synthesis products; duration of hydrothermal synthesis at 150 °C: 1 – 4 h, 2 – 16 h, 3 – 24 h, 4 – 72 h; P – portlandite, Q – quartz, T – 1.13 nm tobermorite, α – α-C₂S hydrate, C – C–S–H(I)

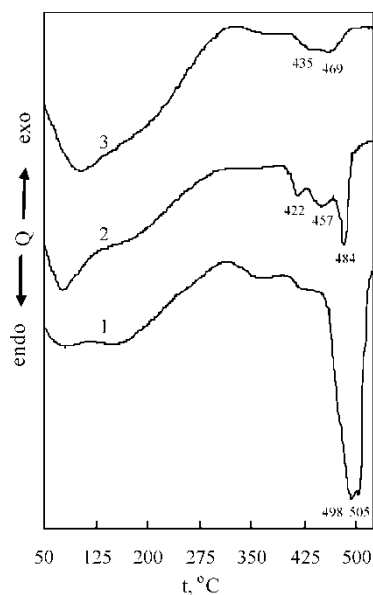


Fig. 2. DSC curves of the synthesis products; duration of hydrothermal synthesis at 150 °C: 1 – 4 h, 2 – 16 h, 3 – 24 h

When hydrothermal synthesis is extended to 16 h, almost all Ca(OH)₂ reacts, and larger quantities of α-C₂S hydrate (Fig. 2, curve 2, endothermic effect at $t = 484$ °C)

and C–S–H(II) (Fig. 1b, curve 2, exothermic peak at $t = 797$ °C) are formed. It should be emphasized that the amount of unreacted quartz decreases. Due to this fact, not only dicalcium silicate hydrates form but also a compound of lower basicity, of C–S–H(I) type calcium silicate hydrate (Fig. 1, curve 2, exothermic peak at $t = 761$ °C). Compared with the pure mixtures, we notice that the shape of the peak corresponding to wollastonite formation ($t = 797$ °C) changes in the DTA curve and shifts towards lower temperatures. Thus, it may be concluded that Na^+ ions accelerate the recrystallization of C–S–H(I) into wollastonite.

When the time of isothermal curing is longer (24 h), $\alpha\text{-C}_2\text{S}$ hydrate and C–S–H(II) are destroyed because more and more quartz dissolves. Instead, 1.13 nm tobermorite and C–S–H(I) are identified in the products (Fig. 1, curve 3, the intensity of exothermic peak increases at 764 °C). However, in mixtures without Na^+ ions, $\alpha\text{-C}_2\text{S}$ hydrate and C–S–H(II), which have not yet decomposed, prevail in the products. It should be noted that quartz does not react completely even after 72 h of synthesis, neither in pure mixtures nor in mixtures with Na_2O (Fig. 1a, curve 4). Thus, at low temperature addition of Na_2O accelerates the transfer of dicalcium silicate hydrates into the compounds of lower basicity, i.e. it stimulates formation of C–S–H(I) and 1.13 nm tobermorite. However, due to a low quartz dissolution rate, the stoichiometric C/S ratio (0.66) of the primary mixture is not reached. It is one of the main reasons why the temperature of 150 °C is too low for the synthesis of low base calcium silicate hydrates (Z-phase, gyrolite) both in pure mixtures and in mixtures with Na_2O additive.

After increasing the temperature to 175 °C, Ca(OH)_2 reacts completely and only semi-crystalline C–S–H(I) is formed in the first 4 h of synthesis (Fig. 3b, curve 1, exothermic peak at 802 °C). Dibasic calcium silicate hydrates are not formed at this temperature. This is partly due to the presence of Na^+ ions in the solution, which accelerate dissolution of quartz by eroding the surface of the particles. After 8 h of synthesis, no essential changes are noticed in the X-ray diffraction pattern and in the DTA curve – an unchanged amount of C–S–H(I) remains, although its molar ratio C/S probably decreases because more quartz reacts (Fig. 3, curve 2). It should be noted that after 72 h of isothermal curing only traces of quartz remain (Fig. 3, curve 3). It was observed that in pure mixtures it is very difficult to dissolve all of the quartz. Approximately, 11% of this compound remained after 168 h at 150 °C, 72 h at 175 °C and 32–72 h at 200 °C [26].

At 175 °C, the formation of 1.13 nm tobermorite is delayed in mixtures containing Na_2O . Traces of this compound are identified only after 72 h of synthesis, while at 150 °C a larger quantity of tobermorite formed after only 24 h. We suppose that it depends on the stability of the compounds that are formed during the first stage of the hydrothermal reactions. This stability is influenced by both temperature and the amount of unreacted quartz. Due to a larger amount of dissolved quartz at 175 °C, the molar ratio C/S in the mixture becomes lower than 0.83 (which corresponds to the stoichiometric composition of 1.13 nm tobermorite) and decreases to the stoichiometric composition (C/S = 0.66) of low base calcium silicate hydrates. Also, it is found

that Na⁺ ions stimulate formation of a new compound (pectolite – Ca₂NaH(SiO₃)₃). After 72 h at 175 °C, pectolite together with traces of tobermorite have been identified in the products (Fig. 3, curve 3). Basic reflections of pectolite (*d*-spacing – 0.2905, 0.2917, 0.3081, 0.3066, 0.3306 nm) are not intense (Fig. 3, curve 3). However, when the synthesis is continued until one week, not only gyrolite and Z-phase but also 1.13 nm tobermorite and pectolite are formed (Fig. 3, curve 4).

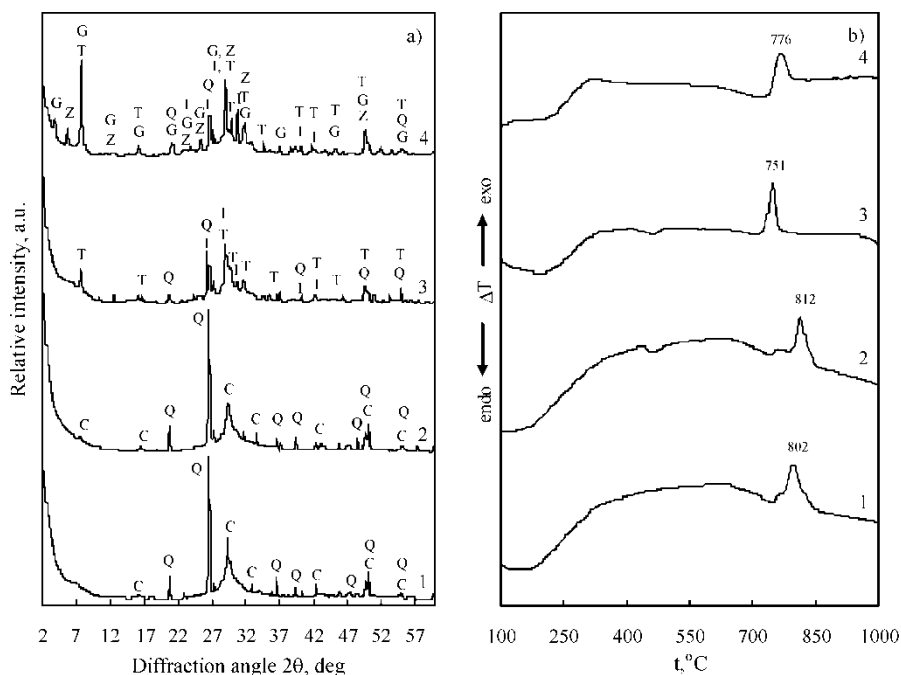


Fig. 3. X-ray diffraction patterns (a) and DTA curves (b) of synthesis products; duration of hydrothermal synthesis at 175 °C: 1 – 4 h, 2 – 8 h, 3 – 72 h, 4 – 168 h; Q – quartz, C – C–S–H(I), Z – Z-phase, G – gyrolite, T – 1.13 nm tobermorite, I – pectolite

On the contrary, when pure mixtures are hydrothermally treated under the same conditions (72 h at 175 °C), quartz, xonotlite, and 1.13 nm tobermorite prevail in the products. As far as we know this is the first evidence that gyrolite can be synthesized when a less active SiO₂ modification – quartz and sodium additive are used. However, a larger quantity of this compound forms only after 168 h of isothermal curing at 175 °C. DTA measurements show a wide exothermic effect at 776 °C, characterizing the transformation of gyrolite into wollastonite (Fig. 3b, curve 4). Moreover, other calcium silicate hydrates are formed together with gyrolite: Z-phase, pectolite, and 1.13 nm tobermorite.

When C–S–H(I) and gyrolite recrystallize into wollastonite, Na₂O reacts as flux (alloying additive), because the exothermic peak, characterizing the formation of wollastonite, significantly shifts towards lower temperatures from 840–860 °C (in pure

mixtures) to 800–750 °C (in mixtures with Na₂O). In order to get the only product of the synthesis – gyrolite – and shorten the time of hydrothermal processing, we increased the temperature of isothermal curing to 200 °C. As expected, just after 4 h a large quantity of semi-crystallized C–S–H(I) was formed (Fig. 4b, curve 1, exothermic peak at 772 °C) and a larger amount of quartz reacted. This is because an endothermic effect at 573 °C was not identified in the DTA curve, and only small intensity peaks, which can be attributed to the quartz, appeared on the X-ray diffraction pattern (Fig. 4a, curve 1).

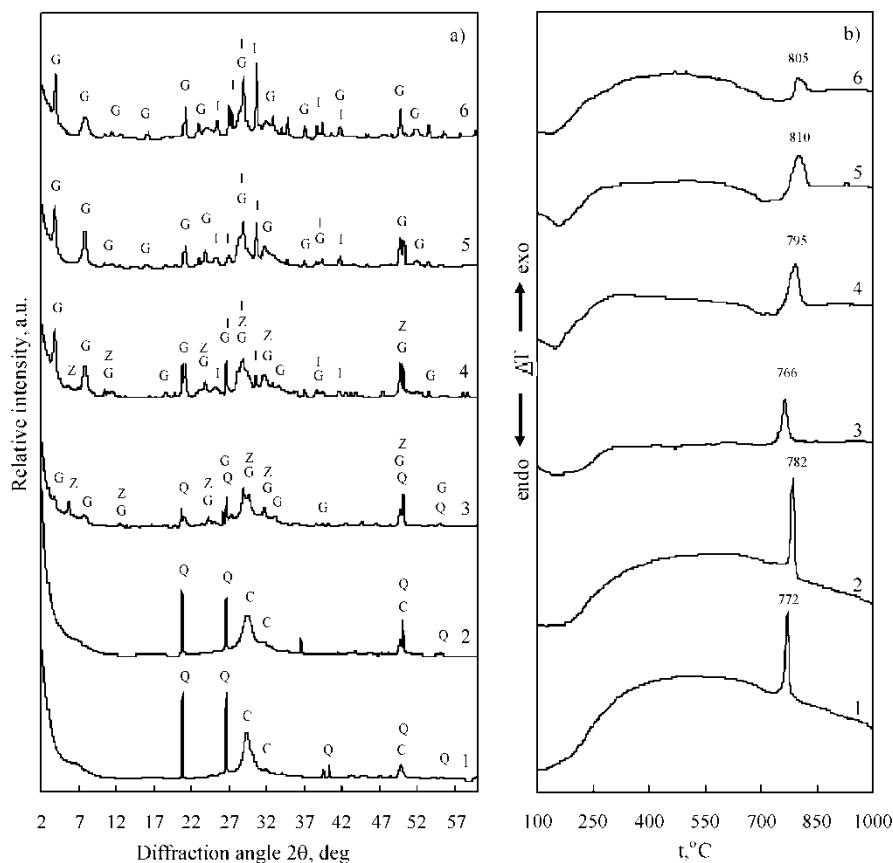


Fig. 4. X-ray diffraction patterns (a) and DTA curves (b) of synthesis products; duration of hydrothermal synthesis at 200 °C: 1 – 4 h, 2 – 8 h, 3 – 16 h, 4 – 24 h, 5 – 32 h, 6 – 168 h; Q – quartz, C – C–S–H(I), Z – Z-phase, G – gyrolite, T – 1.13 nm tobermorite, I – pectolite

When the synthesis is continued, after 8 h the intensity of the basic reflections of quartz slightly decreases. This means that more Si⁴⁺ ions are transferred to the solution and the molar ratio C/S of the mixture becomes closer to the estimated 0.66, creating favourable conditions for the formation of low base calcium silicate hydrates (Fig. 4, curve 2). After a longer time (16 h) almost all quartz reacts. Therefore, it is not a coincidence that basic reflections 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 (Fig. 4a, curve 3). This is confirmed by DTA data as well: the exothermic peak at ~ 782 °C shifts towards lower temperatures (~ 766 °C) and becomes wider (Fig. 4b, curve 3).

As has already been mentioned, in mixtures without Na₂O approximately 11% of quartz does not react even after 72 h of synthesis. The C/S ratio approaches 0.8 and stable calcium silicate hydrates – 1.13 nm tobermorite and xonotlite form. As a result, gyrolite is not formed in those mixtures [26]. Z-phase is not stable in mixtures with a Na₂O. After 24 h of hydrothermal synthesis at 200 °C only traces of this compound remain (Fig. 4, curve 4). Z-phase finishes transferring into new compounds – gyrolite and pectolite – after 32 h of isothermal curing (Fig. 4, curve 5).

In order to examine the stability of both gyrolite and pectolite, we prolonged the time of hydrothermal synthesis up to 48 h. The intensity of the main peak (*d*-spacing 0,291 nm) of pectolite slightly increased, and the intensity of gyrolite (*d*-spacing 2.2 nm) remained unchanged. When the duration of isothermal curing was increased even more (72 h), the quantities of calcium silicate hydrates do not change any more. It is interesting that at 200 °C 1.13 nm tobermorite does not form. One of the main reasons for this is fast dissolution of quartz, which influences the decrease of the C/S ratio and the formation of calcium silicate hydrates, which are stable under these conditions. Thus, at 200 °C, in the system CaO–quartz–Na₂O–H₂O, reactions of formation of gyrolite are quite intensive – it is formed much faster (after 16 h) than at 175 °C (after 168 h). It should be noted that Z-phase and/or pectolite remained and coexisted with gyrolite. If the former compound under given conditions is metastable, then the latter one does not decompose even after 168 h of isothermal curing at 200 °C (Fig. 4, curve 6). It is likely that such reaction mechanism is influenced by Na⁺ ions.

All the data has been confirmed by the IR spectroscopy measurements which may be used to distinguish gyrolite from Z-phase as well as from other calcium silicate hydrates [28, 29]. After comparing the IR spectra of Z-phase and gyrolite it was stated that a weaker band near 595 cm⁻¹ is characteristic of Z-phase when a doublet near 595 and 614 cm⁻¹ is noticed in the IR spectra of gyrolite (Fig. 5, curve 2). The band near approximately 976 cm⁻¹ is more intensive in the IR spectrum of Z-phase (Fig. 5, curve 1) than in gyrolite spectrum (Fig. 5, curve 2). IR spectrum of Z-phase displays a shoulder near 1130 cm⁻¹ corresponding to a strong peak in the spectrum of gyrolite.

A sharp peak near 3635 cm⁻¹ is visible only in the gyrolite spectra (Fig. 5, curves 2–4). This proves that clearly distinguished OH positions exist in the structure of gyrolite which are connected only with Ca atoms being not influenced by hydrogen bridge links. The OH groups are not so well positioned in the Z-phase structure. A wide band near 3446 cm⁻¹ indicates that molecular water forms hydrogen bridges in the interlayers. The bands in the range of 1634 cm⁻¹ are assigned to δ (H₂O) vibrations and confirm this presumption. This peak in the gyrolite spectra is a bit wider (compared with Z-phase or tobermorite), which corresponds to a greater quantity of molecular H₂O in gyrolite structure (Fig. 5, curves 2–4). It is likely that absorption bands in the range of

904 and 926 cm^{-1} are characteristic of pectolite because these peaks were not present in the IR spectra of pure gyrolite. They may be attributed to some modification in the crystal lattice of gyrolite due to intercalation of Na^+ ions into the structure (Fig. 5, curves 3–4).

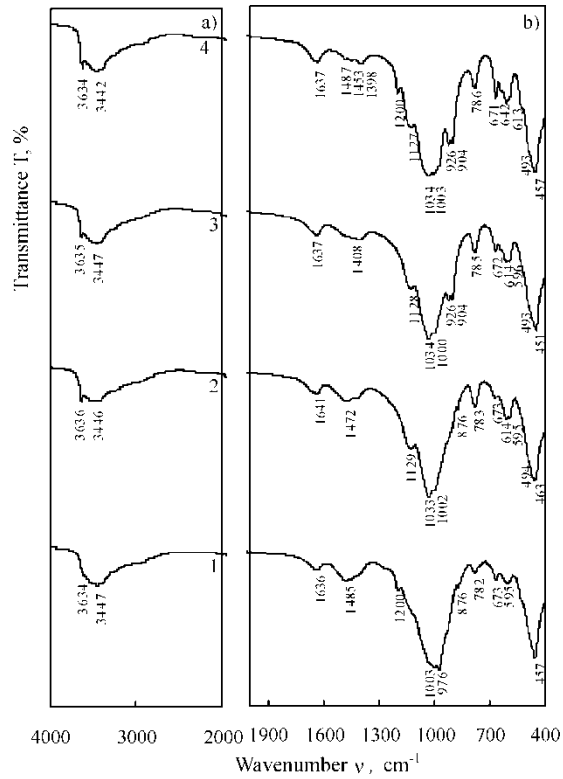


Fig. 5. IR spectra of the synthesis products; duration of hydrothermal synthesis at 200 °C: 1 – 16 h, 2 – 24 h, 3 – 32 h, 4 – 72 h

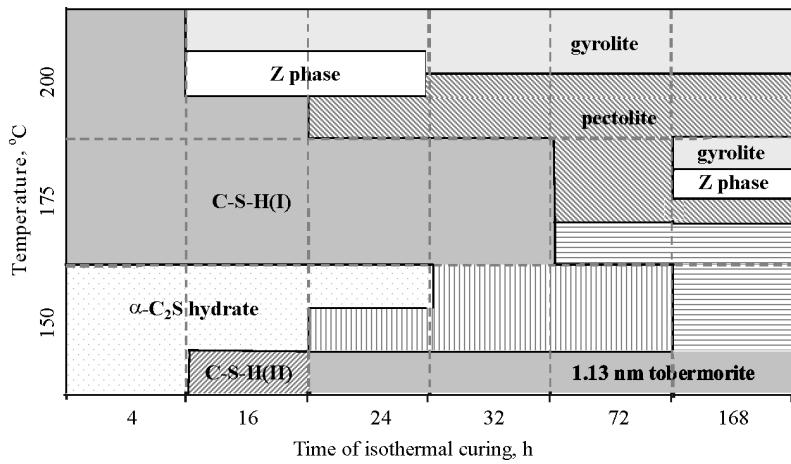


Fig. 6. Dependence of the phase compositions of the products on the temperature and duration of synthesis. Molar ratio of the primary mixture C/S = 0.66, Na_2O content – 5%

The sequence of compounds formed in the synthesis, depending on the temperature and duration of hydrothermal treatment, is demonstrated in Fig. 6. At the beginning of the synthesis α -C₂-S hydrate and C–S–H(II) are formed. They are transferred into compounds of lower basicity – C–S–H(I) and 1.13 nm tobermorite – when the duration and temperature of isothermal curing are increased. Later on, when more and more quartz dissolves, compounds with the stoichiometric composition corresponding to the molar ratio of the primary mixture – Z-phase, gyrolite and pectolite – are formed. The first one exists for a short time, while gyrolite and pectolite remain stable even after 168 h of synthesis at 200 °C.

Acknowledgement

We gratefully thank A. Baltusnikas, the Head of X-ray Diffraction Analysis Laboratory of KTU for carrying out X-ray analysis experiments and for his constructive comments on the paper.

4. Conclusions

The temperature of 150 °C is too low for the synthesis of gyrolite. Due to low quartz dissolution rate, the stoichiometric ratio C/S = 0.66 is not reached even after 168 h of synthesis, neither in pure mixtures nor in mixtures with addition of Na₂O. Na⁺ ions in the CaO–quartz–H₂O mixtures significantly influence the formation of gyrolite in the temperature range from 175 °C to 200 °C. Gyrolite is formed at 175 °C after 168 h and at 200 °C after 16 h of isothermal curing. On the contrary, in pure mixtures gyrolite did not form even after 72 h at 200 °C. Na⁺ ions change the composition of intermediate and final products of the synthesis. In the mixtures with 5% Na₂O, intermediate compounds are C–S–H(I) and Z-phase, and the final products are gyrolite and pectolite. In the mixtures without Na₂O, the main intermediate compounds are α -C₂-S hydrate and C–S–H(II), and the main products are 1.13 nm tobermorite and xonotlite. Na⁺ ions influence the temperature of recrystallization of C–S–H(I) and gyrolite into wollastonite, by reducing it about 50 °C.

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Received 28 June 2007