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Formation of gyrolite during hydrothermal synthesis in the mixtures of CaO and amorphous SiO_2 or quartz

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Abstract

Parameters of gyrolite hydrothermal synthesis were determined when primary mixtures consisting CaO and amorphous $SiO_2 \cdot nH_2O$ or quartz and a sequence of intermediary compound formation were examined and explained. The molar ratio (C/S) of the primary mixtures was 0.66 (C—CaO; S—SiO_2) and the water/solid ratio (W/S) of the unstirred suspension was 10. Hydrothermal synthesis was carried out in saturated steam at 150, 175, and 200 °C temperatures. The duration of isothermal curing was 4, 16, 24, 32, 48, 72, and 168 h.

Gyrolite does not form even after a week in the mixtures of CaO and amorphous SiO_2 at 150 °C temperature in saturated steam. Increase in the temperature positively affects the synthesis of this compound—pure gyrolite at 175 °C was obtained after 72 h at 200 °C—after 32 h. It should be noted that while synthesizing gyrolite, intermediary compounds C-S-H (I) and Z-phase are always formed. The mechanism of hydrothermal reactions and the sequence of compounds to be formed in the mixtures of CaO and quartz are totally different. Due to low quartz solubility rate at temperature range from 150 to 200 °C, neither Z-phase nor gyrolite forms even during 72 h of hydrothermal curing. In the beginning of the synthesis, α-C_2S hydrate prevails, which gradually recrystallizes into 1.13 nm tobermorite and xonotlite. Almost half of the quartz reacts during the first 4 h at 150 °C temperature, and the further decrease of its quantity depends much on the duration of hydrothermal curing. However, about 10% of the quartz does not react at all, when the C/S in the products approach approximately 0.8, stable calcium silicate hydrates—1.13 nm tobermorite and xonotlite—are formed. They are relatively stable. Experimentally obtained data and preconditions were approved by thermodynamic calculations.

Keywords: Gyrolite; 1.13 nm tobermorite; Calcium silicate hydrate; X-ray diffraction

1. Introduction

From a theoretical and practical point of view, the synthesis, properties, and structure of the main calcium silicate hydrates—C-S-H (I), 1.13 nm tobermorite, xonotlite, and α-C_2S hydrate—have been analyzed in detail [1–4]. However, data presented in references about properties of low base compounds ($C/S = 0.6–0.8$) and their formation in hydrothermal conditions are not extensive and often controversial. Of course, it is known that majority of them are occurring naturally or may be synthesized in a laboratory [5–7].

Gyrolite ($2CaO \cdot 3SiO_2 \cdot 2.5H_2O$), a calcium silicate hydrate, rarely occurs as a natural mineral in association with zeolites as a low-temperature hydrothermal replacement product of basic igneous rock. Gyrolite was found for the first time on the Isle of Skye, U.K., by Anderson [8], and it was subsequently identified in several other localities associated with zeolites in basalts. Synthetic gyrolite was hydrothermally synthesized by Flint et al. [9]. They indicated that after 6–42 days of hydrothermal synthesis at 150–350 °C temperature, the only product—gyrolite—forms when C/S changes from 0.5 to 0.66. Mackay and Taylor [10] synthesized this compound at 150 °C temperature within 76 days of isothermal curing.

Later on, other scientists continued the studies on the synthesis of gyrolite [11–13]. It was declared that gyrolite is stable at 120–200 °C temperature in hydrothermal conditions under the saturated steam pressure. Truscottite [$Ca_{14}Si_{24}O_{58}(OH)_8 \cdot 2H_2O$] forms at a temperature higher than 200 °C, although a metastable gyrolite may be obtained up to 270 °C. It is assumed that gyrolite forms only at a temperature higher than 120 °C. At a lower temperature, a semicrystalline having no crystal structure (C-S-H gel) is obtained. At variable C/S, the formation of

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other calcium silicate hydrates, which are stable at the given conditions (pressure, temperature), are produced. Therefore, C-S-H gel is transformed into a semicrystalline C-S-H (I). However, at sufficiently long hydrothermal treatment, this compound may turn into metastable phase, due to the formation of gyrolite. It has been shown that while synthesizing gyrolite, an intermediary compound Z-phase [$Ca_9Si_{16}O_{40}(OH)_2 \cdot (14+x)H_2O$] [14] often forms, with a 1.5-nm basic reflection characteristic.

Recently, Shaw et al. [13] had utilized a synchrotron source of high-energy X-rays and energy-dispersive powder diffraction and presented the information about compound formation sequence in the hydrothermal crystallization of gyrolite at a temperature range of 190–240 °C. They found that Z-phase probably has no stability field, which supports the idea that Z-phase is a transient, metastable phase in the formation of gyrolite.

The structure, optical properties, and chemistry of natural gyrolite were studied by Mackay and Taylor [10], Chalmers et al. [14], Gard et al. [15], Lachowski et al. [16], Merlino [17], and other scientists [12,13]. However, their opinions differ.

In the structural studies of gyrolite, Merlino [17] showed that this phase structure is built up by the stacking of SiO_4 tetrahedral sheets (S_1, S_2, and $\bar{S}_2$, where S_2 and $\bar{S}_2$ are symmetry-related units) and CaO_6 octahedral sheets (O and $\bar{O}$, which are symmetry-related units). The SiO_4 tetrahedra in the silicate sheets are linked by sharing three oxygens, to give a pseudohexagonal sheet structure with tetrahedra in six-membered rings. Each unit cell contains three distinct silicate sheets, two of which (S_2 and $\bar{S}$) are symmetrically equivalent with the six-membered rings having four tetrahedra pointing one way and two the other; the third sheet (S_1) has alternate tetrahedra six-membered rings pointing in opposite directions. These sheets are linked by layers of Ca–(O,OH) polyhedra to build up a "complex layer" perpendicular to *c* axis. The stacked complex layers ($\bar{S}_2$ $\bar{O}$ S_1 O S_2) with composition $[Ca_7Si_{12}O_{30}(OH)_4]^{2-}$ are connected through interlayer sheets made by Ca^{2+} ions and water molecules.

The results published in the references do not allow for precise determination of gyrolite synthesis conditions. In addition, we have failed in finding some data about gyrolite formation in the mixtures of CaO and quartz, which form a sequence of new formations. Meanwhile, it is known that 1.13 nm tobermorite is easier to be synthesized in the mixtures with quartz than with amorphous SiO_2 [18]. Thus, it might be presumed that in the mixtures with quartz gyrolite will be easily formed.

Synthesis and properties of minerals from tobermorite group are widely analyzed. However, gyrolite has been analyzed considerably less. One of the reasons why synthesis and properties of gyrolite are not analyzed in detail is the fact that this compound is still rarely applied in practice. As it results from some published works, it is suitable for water cleaning from heavy metal ions [19], and it is known for its selectivity to DNA [20].

The aim of this paper is to determine the parameters of gyrolite hydrothermal synthesis when the primary mixtures are formed from CaO and amorphous $SiO_2 \cdot nH_2O$ or quartz as well as to analyze and explain the sequence of intermediary compound formation.

2. Materials and methods

In this paper, the following reagents were used as starting materials: fine-grained $SiO_2 \cdot nH_2O$ (ignition losses 21.43%, specific surface area (S) = 1560 m^2/kg by Blaine); fine-grained quartz (of specific surface 1100 m^2/kg), after grinding washed away iron impurities by hydrochloric acid; and calcium oxide (of specific surface 548 m^2/kg) which has been produced by burning calcium carbonate at 1000 °C for 6 h.

The synthesis of calcium silicate hydrates has been carried out in unstirred slurries. C/S of primary mixture was 0.66. Dry primary mixtures have been mixed with water in the vessels of stainless steel (suspension W/S = 10.0). Hydrothermal synthesis has been carried out under the saturated steam pressure at temperatures 150, 175, and 200 °C; the duration of isothermal curing was 4, 16, 24, 32, 48, 72, or 168 h. The products of the synthesis have been filtrated, rinsed with ethyl alcohol to prevent carbonization of material, dried at temperature of 100 ± 5 °C, and sieved through sieve no. 008.

The X-ray powder diffraction data were collected with DRON-6 powder X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with voltage 30 kV and emission current of 20 mA. The step scan covered the angular range $5-60^\circ$ (2θ) in steps of $2\theta = 0.02^\circ$. Diffraction curves were additionally recorded in step times 1.0 s and step size of 0.01° (2θ) from 2° to 10°. For diffraction profile refinement under the pseudoVoid function and for description of the diffractional background under the third-degree Tchebyshev polynom, we used a computer program X-fit [21]. Thermal analyzer DuPont 990 (USA) with computerized control and data recording was applied for differential thermal analysis (DTA) studies. The heating was carried out in air—the rate of temperature increase was 10 °C/min, and the temperature ranged from 100 up to 1000 °C. The ceramic sample handlers and Al_2O_3 as inert material were used. The specific surface area of the raw materials was determined by the Blaine's method. The free CaO content in the products was determined by the glicol method.

3. Results and discussions

The formation of crystalline calcium silicate hydrates (Z-phase, gyrolite) at 150 °C in CaO mixtures with amorphous SiO_2 goes very slowly. After 24 h of hydrothermal curing, X-ray diffraction patterns show basic reflections characteristic only for C-S-H gel (Fig. 1, Curve 1, d-spacing—0.5451, 0.3062, and 0.1838). C/S in this material (according to Taylor) is equal to 1.3–2.0 [22]. Further on, d-spacing increases, and C-S-H (I) is formed. The C/S of this product, following the reference data [23], decreases from 1.3–2.0 to 0.8–1.3.

Gyrolite did not form even after 1 week of hydrothermal curing at a considerably low temperature of isothermal curing (150 °C) (Fig. 1, Curve 2). Z-phase (d-spacing—1.5560, 0.8404, 0.4167, 0.3705, 0.3058, 0.2795, and 0.1836 nm) was dominant in the products together with a semi-crystalline C-S-H (I)-type calcium silicate hydrate (d-spacing—1.2440, 0.3048, 0.2796, and 0.1832 nm). In the beginning of the synthesis, the compounds with a higher C/S are formed, due to the fact that the initial solution contains excess of CaO. When the synthesis is continued, the basicity of compounds to be formed reduces, C/S approaches the calculated composition (C/S = 0.66); therefore, Z-phase starts to prevail in the products. Thus, 150 °C temperature is too low for gyrolite formation.

When the temperature of synthesis is increased up to 175 °C, the reactions between CaO and amorphous SiO_2 are more intensive—the main Z-phase peak at 1.5 nm is identified already after 24 h of hydrothermal curing (Fig. 1, Curve 3), and after 48 h, the traces of gyrolite are found (Fig. 1, Curve 4). One can notice that the Z-phase at 175 °C temperature remains stable only within 2 days than at 150 °C temperature (when it occurs up to 1 week).

It was observed also that in the presence of Z-phase, a nature of calcium silicate hydrates recrystallizing into wollastonite changed as it could be found from the DTA curve. The exothermic peak attributed to wollastonite synthesis changed, that is, it became wider and moved towards higher temperatures (Fig. 1b, Curves 2–4).

During a 72-h synthesis at 175 °C, Z-phase transforms into gyrolite (Fig. 1, Curve 5; d-spacing—2.2810, 1.1262, 0.8371, 0.4197, 0.3732, 0.3511, 0.2803, and 0.2141). We can see this as the most characteristic peak of Z-phase at 1.5 nm, which is not characteristic to other calcium silicate hydrates, disappears and the intensity of the most characteristic peak of gyrolite at 2.2 nm increases.

Thus, although gyrolite already forms at 175 °C temperature, crystallization is slow and takes about 72 h.

The reference data already presented [9,12] do not allow the determination of the start of gyrolite formation and the end of its transformation into other compounds. The main reason is that the peaks of this compound coincide with those of other calcium silicate hydrates. The most characteristic d-spacing of gyrolite (d = 2.2 nm) is very close to a zero 2θ angle, i.e., to a falling radius, which, using a standard radius focus, "covers" this peak. Therefore, to "separate" this peak in X-ray radius focus, we used a special collimator and graphite monochromator. This enabled us to find out whether gyrolite has been formed during synthesis or not.

At 200 °C, the reactions of calcium silicate hydrates occur intensively. After 16 h of hydrothermal curing, well-crystallized Z-phase crystals and C-S-H (I)-type

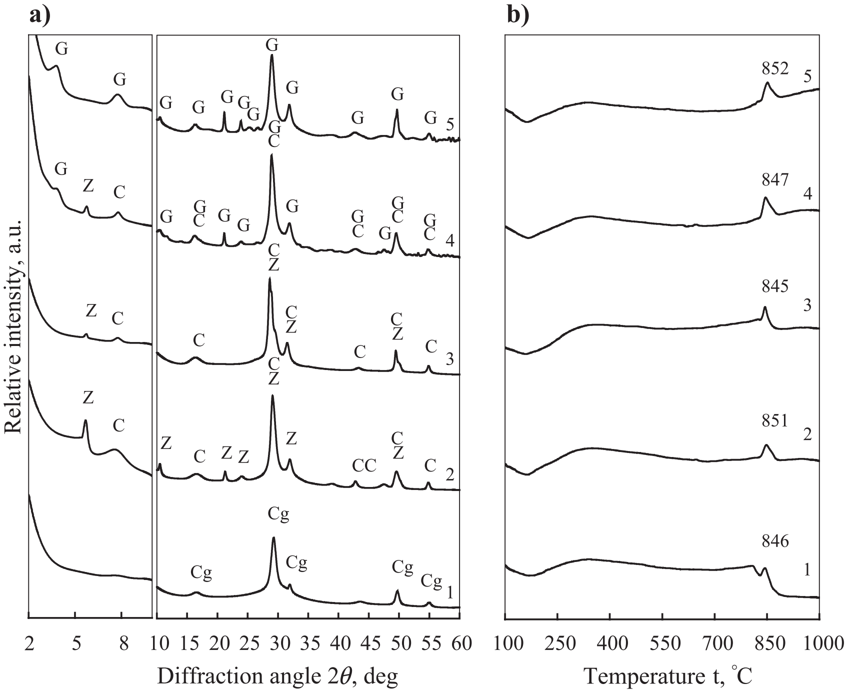


Fig. 1. X-ray diffraction patterns (a) and DTA curves (b) of synthesis products at different temperatures and durations of hydrothermal curing: 1—150 °C, 24 h; 2—150 °C, 168 h; 3—175 °C, 24 h; 4—175 °C, 48 h; 5—175 °C, 72 h. SiO_2 component—$SiO_2 \cdot nH_2O$. Cg—C-S-H gel, C—C-S-H (I), Z—Z-phase, G—gyrolite.

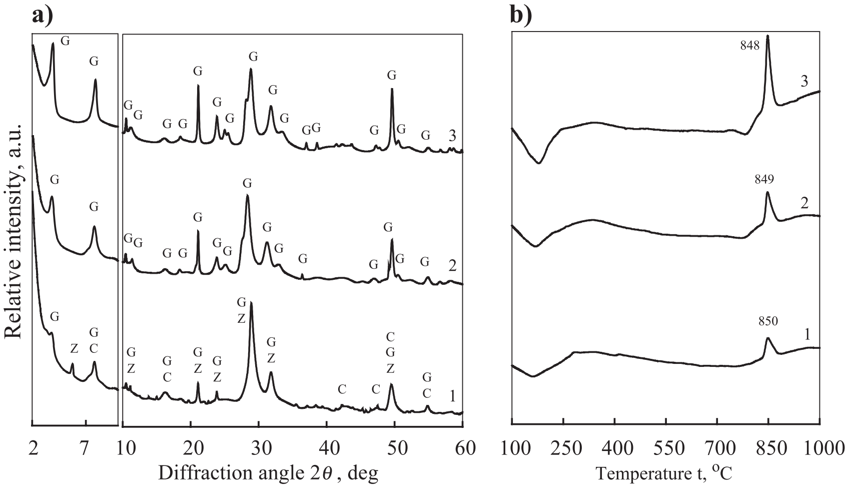


Fig. 2. X-ray diffraction patterns (a) and DTA curves (b) of synthesis products. Duration of hydrothermal synthesis at 200 °C temperature: 1—16 h; 2—32 h; 3—72 h. SiO_2 component—$SiO_2 \cdot nH_2O$. Z—Z-phase, G—gyrolite, C—C-S-H (I).

calcium silicate hydrate already form, and some amount of gyrolite crystals are noticed (Fig. 2, Curve 1). It should be underlined that Z-phase at 200 °C temperature transforms into gyrolite (approximately 32 h) (Fig. 2, Curve 2) considerably quicker than at 175 °C temperature (approximately 72 h). Presented data show that while synthesizing gyrolite, Z-phase is an intermediary compound. In addition, intensity of Z-phase peaks, except that of 1.5 nm, increases when Z-phase turns into gyrolite at 200 °C temperature; gyrolite still remains to be the only compound after either 48 or 72 h of hydrothermal synthesis (Fig. 2, Curve 3). Moreover, attention should be paid towards the fact that when Z-phase transforms into gyrolite, the nature of wollastonite formation peak

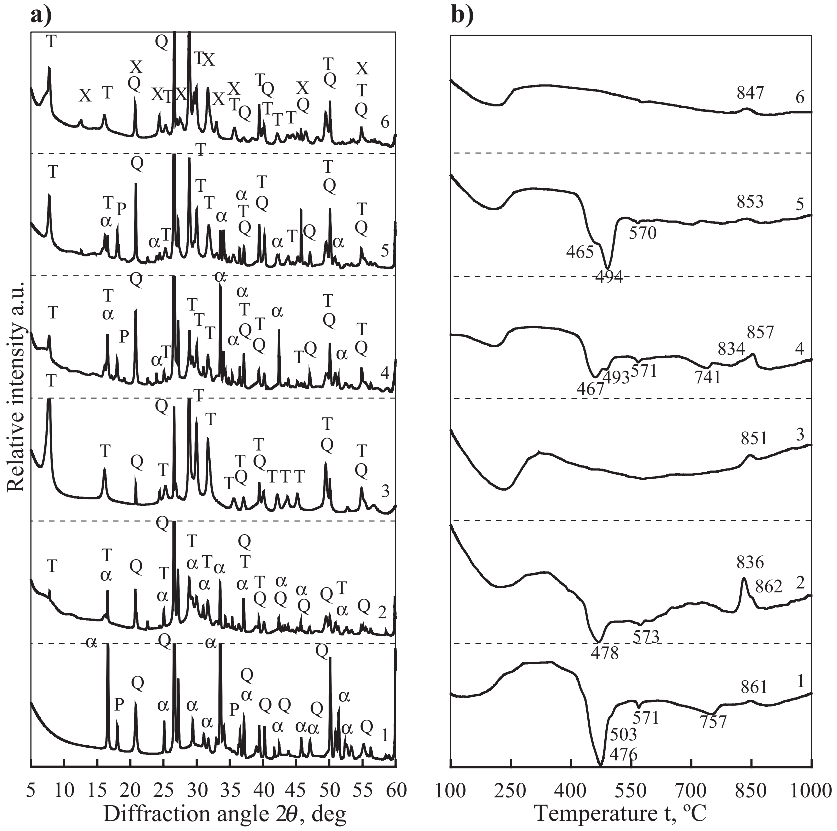


Fig. 3. X-ray diffraction patterns (a) and DTA curves (b) of synthesis products at different temperature and duration of hydrothermal curing: 1—150 °C, 24 h; 2—150 °C, 48 h; 3—150 °C, 168 h; 4—175 °C, 16 h; 5—175 °C, 32 h; 6—175 °C, 48 h. SiO_2 component—quartz. α—α-C_2S hydrate; P—portlandite; Q—quartz; T—1.13 nm tobermorite; X—xonotlite.

changes in the DTA curve—it becomes higher and sharper (Fig. 2b, Curves 1–3).

It is possible to assume that when curing the mixture of CaO and amorphous SiO_2 at 150–200 °C temperature under the saturated steam pressure, the reactions of new compounds formation occur in the following sequence:

$$Ca(OH)_2 + SiO_2\ nH_2O + H_2O \rightarrow C - S - H\ \text{gel}$$

$$\rightarrow C - S - H\ (I) \rightarrow Z - \text{phase} \rightarrow \text{gyrolite}$$

It should be stressed that the mechanism of hydrothermal reactions and the sequence of the compounds formed in CaO mixtures with quartz are quite different, as quartz reacts considerably slower than $SiO_2{\cdot}nH_2O$, and the solution contains a significant excess of Ca^{2+} ions. Due to this reason, compounds with a higher C/S than it has been expected under a stoichiometric composition of the initial mixture are formed. This was confirmed by X-ray diffraction and DTA data. After 24 h of isothermal curing at 150 °C, the calcium silicate hydrates, α-C_2S (d-spacing—0.5330, 0.3547, 0.2847, 0.2665, 0.2489, 0.2176, and 0.1779 nm; temperature of the endothermic effect $t = 503$ °C), C-S-H (II) ($t = 861$ °C) form, and large quantities of $Ca(OH)_2$ residue (d-spacing—0.4908; 0.2635 nm, $t = 476$ °C) and quartz (d-spacing—0.425, 0.334, 0.245, and 0.228 nm; $t = 571$ °C), remain (Fig. 3, Curve 1).

When the hydrothermal synthesis is extended to 48 h, a considerably larger part of quartz and almost all $Ca(OH)_2$ react, almost all α-C_2S hydrate decomposes, and C-S-H (I) forms (Fig. 3, Curve 2; exothermic effect at 836 °C temperature). However, if the synthesis is continued (to 168 h), 1.13 nm tobermorite starts to prevail in the product (Fig. 3a, Curve 3). Thus, at 150 °C in CaO and quartz mixtures, the α-C_2S calcium silicate hydrate is a dominant product at the beginning of the reaction and subsequently transforms into 1.13 nm tobermorite with time. Compounds to be expected at C/S = 0.66 (Z-phase, gyrolite) do not form due to the low quartz solubility rate. The C/S in the products is higher and close to that of 1.13 nm tobermorite (0.83).

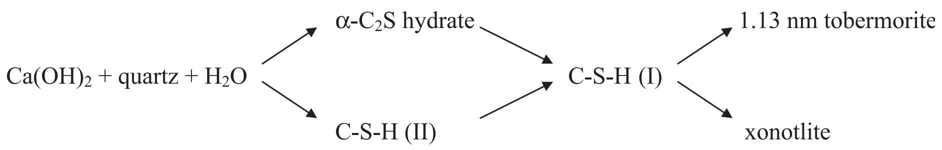
To increase reaction rate and avoid the formation of dicalcium silicate hydrates, hydrothermal synthesis were carried out at higher temperatures. At 175 °C after 16 h of synthesis, α-C_2S hydrate, $Ca(OH)_2$, C-S-H (II), and traces of 1.13 nm tobermorite form (Fig. 3, Curve 4). At prolonged time up to 32 h, C-S-H (I) forms together with C-S-H (II) Fig. 3b, Curve 5; exothermic peak at 853 °C temperature). It was unexpected that after 32 h of hydrothermal curing, the intensity of α-C_2S hydrate peaks in X-ray diffraction pattern decreases, and the endothermic effect in DTA curve increases (Fig. 3, Curve 5).

In 1974, Taylor [6] has already noted that at temperatures higher than 150 °C, tobermorite is thermodynamically unstable in the mixtures with C/S>0.8.

Thus, due to a low quartz solubility rate, C/S is higher than 0.66, even in the mixture reacting at 175 °C temperature. Therefore, at sufficiently long hydrothermal curing (48 h), tobermorite transforms into xonotlite (Fig. 3, Curve 6; d-spacing—0.7064, 0.4279, 0.3663, 0.3216, 0.2816, and 0.1832), not gyrolite.

It should be pointed out that at 200 °C, neither dicalcium silicate hydrates, α-C_2S hydrate, nor C-S-H (II) form. After 16 h of isothermal curing, xonotlite forms together with 1.13 nm tobermorite. At a longer time of synthesis, the quantity of the latter compound increases a little. It should be noted that quartz does not dissolve even during 72 h, and the quantity of 1.13 nm tobermorite changes unevenly—increases and decreases. We suppose that it is related to the change in the C/S during the synthesis.

Thus, in CaO–quartz–H_2O system, due to a low quartz solubility rate at the temperature range from 150 to 200 °C, neither Z-phase nor gyrolite forms even during 72 h of hydrothermal curing. The sequence of compounds to be formed during the synthesis looks as follows:



Reactivity of the primary mixture components is one of the most important factors, which predetermine mineral composition of the products. Quartz solubility rate is a limiting factor; therefore, we approximately determined the quantity of unreactant quartz by using X-ray diffraction analysis method, and we calculated the C/S of the reactive mixture. While calculating, we considered how much of unreacted $Ca(OH)_2$ remains. Quartz quantity was calculated from the intensity change of the basic reflection (0.334 nm). Each calculation was done five times, and it was determined that their data declined no more than ± 5% from the mean. Quartz quantity in the primary mixture (C/S = 0.66) was equal to 100%.

As it results from the data shown in Fig. 4 at low temperature (150 °C), almost half of quartz reacts

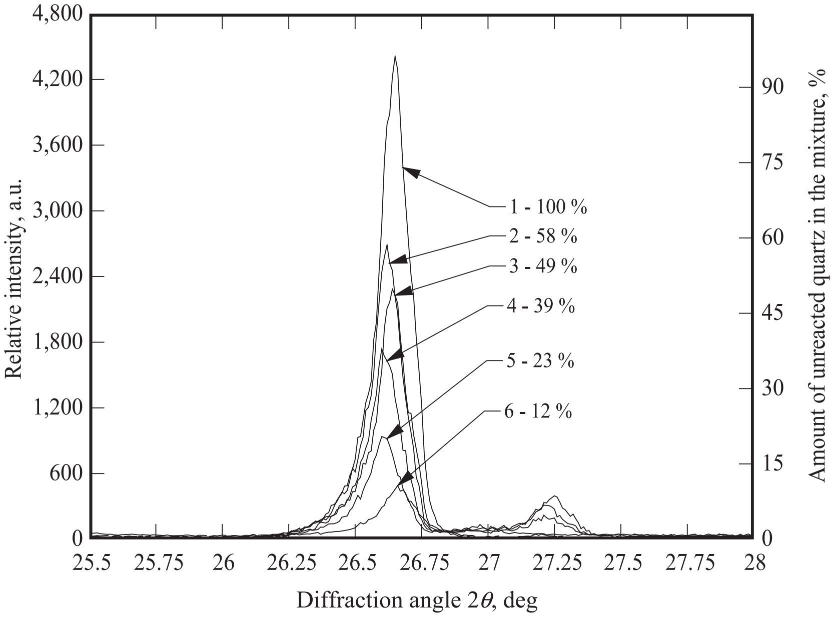


Fig. 4. Quartz residue quantity (%) and change of its basic reflection at 150 °C temperature at different durations of isothermal curing: 1—quartz quantity in primary mixture equal to 100%; 2–4, 3–16, 4–24, 5–48, and 6–168 h.

during the first 4 h of synthesis, and the further reduction of its quantity depends on duration of hydrothermal curing.

At higher temperatures (175 or 200 °C), quartz reacts considerably quicker, and about 75–80% of it is bound during 16 h of isothermal curing (Table 1).

It was noticed that the last 10% of quartz reacts very slowly. It was determined that almost the same quantity of quartz remains after 168 h (150 °C), 72 h (175 °C), and 32–72 h (200 °C). Remains of quartz do not react as the C/S of the products approaches 0.8 (Table 2) and stable calcium silicate hydrates, 1.13 nm tobermorite and xonotlite, are formed.

It should be underlined that the calculated C/S of the primary mixture (0.66) cannot be reached in the products even after 1 week of isothermal curing. This is the reason why gyrolite does not form during synthesis and 1.13 nm tobermorite and xonotlite are variable. In addition, it is obvious that at the beginning of the synthesis, the favourable conditions for the formation of dicalcium silicate hydrates experimentally approved occur. Later, when quartz dissolves, the C/S of the mixture decreases. Therefore, α-C_2S hydrate and C-S-H (II) become unstable and transform into stable phases that is calcium silicate hydrates (1.13 nm tobermorite and xonotlite) of an appropriate stoichiometry.

Table 1
Quartz residue quantity (%), as a function of time and temperature of hydrothermal synthesis

Temperature (°C)	Time of isothermal curing (h)				
	16	24	32	48	72
175	26%	22%	19%	15%	14%
200	22%	15%	11%	12%	11%

Experimental data and theoretical hypothesis were also approved by thermodynamic calculations. They were carried out using V. I. Babushkin et al. method [24]. Primary data is taken from the database [24,25]. The C/S (SiO_2 component—quartz) of the mixtures were the following:

- 0.66—corresponds gyrolite stoichiometry;
- 0.83 (0)—ratio most often obtained during our work (Table 2);
- 1.33—ratio in the beginning of the synthesis.

When C/S = 0.66,

1. $2Ca(OH)_2 + 3SiO_2 + H_2O* \rightarrow 2CaO \cdot SiO_2 \cdot 1.17\,H_2O + 2SiO_2 + 1.83H_2O$α-$C_2S$ hydrate
2. $2Ca(OH)_2 + 3SiO_2 + H_2O \rightarrow 0.4(5CaO \cdot 6SiO_2 \cdot 5.5H_2O) + 0.6SiO_2 + 0.8H_2O$ Tobermorite

Table 2
C/S of the products as a function of time and temperature of isothermal curing

Temperature (°C)	Time of isothermal curing (h)						
	4	16	24	32	48	72	168
150	1.33	1.26	1.06	–	0.84	–	0.73
175	–	0.87	0.83	0.80	0.76	0.75	–
200	–	0.83	0.76	0.73	0.74	0.73	–

SiO_2 component—quartz.

3. $2Ca(OH)_2 + 3SiO_2 + H_2O \rightarrow 0.333(6CaO \cdot 6SiO_2 \cdot H_2O) + SiO_2 + 2.67H_2O$ Xonotlite
4. $2Ca(OH)_2 + 3SiO_2 + H_2O \rightarrow CaO \cdot 2SiO_2 \cdot 2H_2O + Ca(OH)_2 + SiO_2$ Z-phase
5. $2Ca(OH)_2 + 3SiO_2 + H_2O \rightarrow 2CaO \cdot 3SiO_2 \cdot 2.5H_2O + 0.5H_2O$ Gyrolite

Note: The symbol (*) above denotes that one mole of H_2O was chosen, as during the fifth reaction, all starting materials [$2Ca(OH)_2$ and $3SiO_2$] theoretically react, and only the main synthesis product, gyrolite, forms.

Dependencies of Gibbs free energy values on temperature are shown in Fig. 5.

Fig. 5 clearly shows that during the reaction in the system $Ca(OH)_2–SiO_2–H_2O$, there is the greatest possibility that gyrolite will be one of the main compounds in the products (when C/S = 0.66), as the obtained Gibbs free energy value of this compound is the least one (Fig. 5a, Curve 2). It should be noted that the formation of α-C_2S hydrate in such conditions is the least probable, and it still decreases with increasing temperature (Fig. 5a, Curve 1).

From a thermodynamic point of view, when C/S = 0.83, 1.13 nm tobermorite should dominate at the initial stage of the synthesis and transforms into xonotlite later on (Fig. 5b).

It was noticed that when increasing the C/S of the mixture (Fig. 5c), the probability of α-C_2S hydrate formation also increases, and xonotlite should start to dominate at lower temperatures. Meanwhile, the possibility of low-base calcium silicate hydrates (Z-phase, gyrolite) formation decreases (Fig. 5c, Curves 2 and 5).

Thus, when changing C/S and synthesis conditions (duration, temperature, and other parameters of hydrothermal curing), there is a possibility to obtain stable calcium silicate hydrates.

4. Conclusions

Gyrolite does not form even during a week in the mixtures of CaO and amorphous SiO_2 at 150 °C under the saturated steam pressure. The temperature increase positively affects the synthesis of this compound—pure gyrolite is produced at 175 °C after 72 h and at 200 °C after 32 h. It should be noted that while synthesizing gyrolite, the intermediary compounds, C-S-H (I) and Z-phase, are always formed.

Mechanism of hydrothermal reactions and a sequence of compounds to be formed in CaO mixtures with quartz are quite different. Due to a low quartz solubility rate at a temperature range of 150–200 °C, neither Z-phase nor gyrolite is formed even after 72 h of hydrothermal curing. The dicalcium silicate hydrates, α-C_2S hydrate and C-S-H (II) prevail in the beginning of the synthesis and gradually recrystallizes into 1.13 nm tobermorite and xonotlite.

At 150 °C temperature, almost half of the quartz reacts during the first 4 h, and a further decrease in its quantity

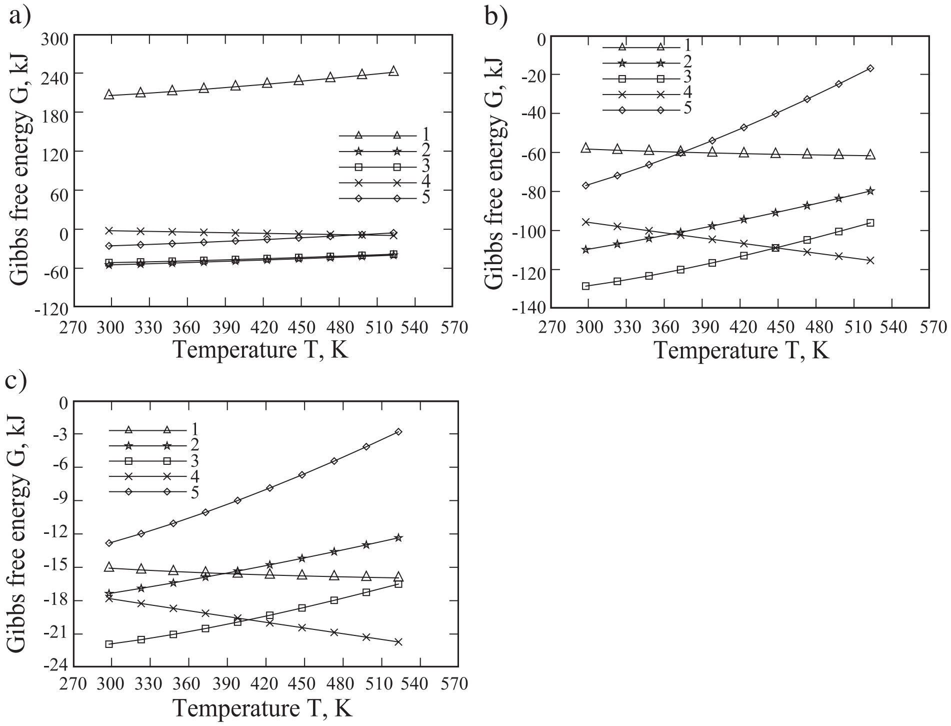


Fig. 5. Gibbs free energy values as a function of temperature when the C/S of the primary mixture is equal to 0.66 (a), 0.83 (b), or 1.33 (c). 1—α-C_2S hydrate; 2—gyrolite; 3—1.13 nm tobermorite; 4—xonotlite; 5—Z-phase.

depends much on the time of hydrothermal curing. However, about 10% of the quartz does not react at all. When C/S approaches 0.8, stable calcium silicate hydrates, 1.13 nm tobermorite and xonotlite, form.

Experimentally obtained data are verified by thermodynamic calculations.

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References

[1] H.D. Megaw, C.H. Kesley, Crystal structure of tobermorite, Nature 177 (1956) 390–391.

[2] S. Merlino, E. Bonaccorsi, T. Armbruster, The real structures of tobermorite 11 Å: OD character and polytypic modifications, Eur. J. Mineral. 13 (2001) 577–590.

[3] G.L. Kalousek, T. Mitsuda, H.F.W. Taylor, Xonotlite: cell parameters, thermogravimetry and analytical electron microscopy, Cem. Concr. Res. 7 (3) (1977) 305–312.

[4] R.E. Marsh, A. Revised, Structure for a-dicalcium silicate hydrate, Acta Crystallogr. 50 (1994) 996–997.

[5] K. Garbev, L. Black, G. Beuchle, P. Stemmermann, Inorganic polymers in cement based materials, Wasser Geotechnol. 1 (2002) 19–30.

[6] H.F.W. Taylor, Crystal chemistry of Portland cement hydration, 6th International Congress on the Chemistry of Cement, vol. 43, Research Institute VNIIESM of the Ministry of Building Materials Industry of the former USSR, Moscow, 1974.

[7] H.F.W. Taylor, Cement Chemistry, Academic Press, San Diego, CA, 1997.

[8] T. Anderson, Gyrolite, Philos. Mag. Sect. IV (1) (1851) 111–115.

[9] E.P. Flint, H.F. McMurdie, L.S. Wells, Formation of hydrated calcium silicate as elevated temperatures and pressures, J. Res. Natl. Bur. Stand. 21 (1938) 617–638.

[10] A.L. Mackay, H.F.W. Taylor, Gyrolite, Mineral. Mag. 30 (1953) 80–91.

[11] L. Števula, M. Harman, I. Horvath, K. Putyera, The mineral gyrolite and its stability under hydrothermal conditions, Ceram.-Silik. 34 (1990) 315–330.

[12] R. Jauberthie, M. Temimi, M. Laquerbe, Hydrothermal transformation of tobermorite gel to 10 Å tobermorite, Cem. Concr. Res. 26 (9) (1996) 1335–1339.

[13] S. Shaw, C.M.B. Henderson, S.M. Clark, In-situ synchrotron study of the kinetics, thermodynamics, and reaction mechanism of the hydrothermal crystallization of gyrolite $Ca_{16}Si_{24}O_{60}(OH)_8 \cdot 14H_2O$, Am. Mineral. 87 (2002) 533–541.

[14] R.A. Chalmers, V.C. Farmer, R.I. Harker, S. Kelly, H.F.W. Taylor, Mineral. Mag. 33 (1964) 821–840.

[15] J.A. Gard, T. Mitsuda, H.F.W. Taylor, Some observations on Assarsson's Z-phase and its structure relations to gyrolite, truscottite and reyerite, Mineral. Mag. 43 (1975) 325–332.

[16] E.E. Lachowski, L.W. Murray, H.F.W. Taylor, Truscottite: composition and ionic substitutions, Mineral. Mag. 43 (1979) 333–336.

[17] S. Merlino, Gyrolite: its crystal structure and crystal chemistry, Mineral. Mag. 52 (1988) 377–387.

[18] W. Nocun-Wczelik, Effect of some inorganic admixtures on the formation and properties of calcium silicate hydrates produced in hydrothermal conditions, Cem. Concr. Res. 27 (1) (1997) 83–92.

[19] M. Miyake, M. Iwaya, T. Suzuki, Aluminum-substituted gyrolite as cation exchanger, J. Am. Ceram. Soc. 73 (11) (1990) 3524–3527.

[20] M.A. Winters, J.D. Richter, S.L. Sagar, A.L. Lee, R.J. Lander, Plasmid DNA purification by selective calcium silicate adsorption of closely related impurities, Biotechnol. Prog. 19 (2003) 440–447.

[21] R.W. Cheary, A.A. Coelho, Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England, (1996) (http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm).

[22] K. Mohan, H.F.W. Taylor, University of Aberdeen, Old Aberdeen, Scotland, ICDD Grant-in-Aid, 1980.

[23] H.F.W. Taylor, University of Aberdeen, Old Aberdeen, Scotland, ICDD Grant-in-Aid, 1980.

[24] V.I. Babushkin, G.M. Matveev, O.P. Mchedlow-Petrossyan, Thermodynamics of Silicates, 4th ed., Stroyizdat, Moscow, Russia, 1986. In Russ.

[25] http://tigger.uic.edu/~mansoori/Thermodynamic.Data.and.Property_html.