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The influence of γ-Al_2O_3 and Na_2O on the formation of gyrolite in the stirring suspension

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Abstract Influence of γ-Al_2O_3, Na_2O and hydrothermal synthesis parameters on the gyrolite formation process was established at 200 °C. The molar ratios of 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 from the mass of dry materials, added in the form of solution. It was determined that in the stirred suspensions under favourable synthesis conditions (active SiO_2 component, dispersive starting materials) gyrolite already forms after 16 h of isothermal curing at 200 °C. The stirring affects the sequence of intermediate compounds: gyrolite crystallizes together with Z-phase. γ-Al_2O_3, as the additive in gyrolite synthesis is not usable, because it stimulates other calcium silicate hydrates formation. Na_2O additive positively affects gyrolite synthesis because the duration of gyrolite synthesis shortens almost 2–3 times (6 h, 200 °C) to compare with pure mixtures. However, gyrolite is not stable in the mixture with Na_2O and begins to turn into pectolite already after 16 h of isothermal curing. Moreover, the presence of (Na_2O + γ-Al_2O_3) additive stabilizes gyrolite and prevents its transformation to pectolite. Obtained results were confirmed by XRD, DSC and SEM/EDS analysis methods.

Introduction

Calcium silicate hydrates—C-S-H(I), 1.13 nm tobermorite, xonotlite, α-C_2S hydrate, gyrolite, and others, or combinations of co-existing phases have been surprisingly found to impart properties which make the cement particularly well suited for the use under conditions of high temperatures, high pressures, and corrosive environments, that occur in deep oil wells and in geothermal wells [1]. The synthesis, properties and structure of the mentioned calcium silicate hydrates have been analyzed in detail. 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 [2–4].

The mineral gyrolite was first discovered on the Isle of Skye by T. Anderson (1851), who quoted a composition of $Ca_2Si_3O_8 \cdot 3H_2O$ [5]. Subsequently gyrolite together with the other minerals has been found at other localities: Germany (Rheinland-Pfalz), India (Maharastra), Russia (Ural), United States of America (Oregon, Virginia) [6–9]. In nature gyrolite often forms nodular aggregates. The aggregate nodules can often accompany many fine and rare minerals such as apophyllite, okenite and many of the zeolites. Much gyrolite forms inside of volcanic bubbles called vesicles and can only add another element to the surreal ‘‘landscape’’ inside [10, 11].

E. P. Flint et al. (1938) were the first that synthesized gyrolite in laboratory [12], later on other scientists made this also [13–17]. The parameters of gyrolite hydrothermal synthesis in the unstirred suspensions when initial mixtures composed from CaO and $SiO_2 \cdot nH_2O$ or quartz were observed in the previous work [18]. The results of the research showed that optimal temperature of gyrolite synthesis is rather high (approximately 200 °C) and the duration are long (about 32 h) when amorphous $SiO_2 \cdot nH_2O$ is used as SiO_2 component. Often it is stated that the crystal

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lattice of the gyrolite found in nature always has both sodium and aluminium ions. This presumption has been confirmed by many tests of S. Merlino who indicated the most likely composition of gyrolite found in nature: Na-$Ca_{16}Si_{23}Al_{60}(OH)_8 \cdot 14H_2O$ [19]. Recently A. Stumm et al. (2004) have indicated that zinc incorporation into synthetic gyrolite is also possible up to Zn/(Zn+Ca) = 1/6, corresponding to approximately 6 wt.%. Increasing zinc content led to a gradual diminishing of the basal reflection (001) of gyrolite, as for the nanocrystalline phases [20]. Currently S. Shaw et al. (2002) having used one of the newest research methods (the synchrotron X-ray radiation source of high energy) have explored the mechanical, kinetic, and energetic processes that are proceeding during the formation of gyrolite [21].

The new possibilities of gyrolite application were found during the last years. The purported ability of gyrolite to separate supercoiled plasmid, opencircular plasmid, and genomic DNA are of specific interest. Use of gyrolite provides a method to simplify that process because the material has been shown to absorb selectively open-circular plasmid and genomic DNA from supercoiled plasmid [22]. Lately the industrial manufacturing of disposable rotary drum filter for DNA separation was started [23]. Also, it is known that Al-substituted gyrolite may be used to educe heavy metal ions and remove them from waste waters [24, 25].

In order to use more broadly gyrolite in practice the manufacturing of this material must be cut in price, i.e., to reduce the duration of hydrothermal treatment and/or the temperature. The attempts to intensify the gyrolite formation reactions in the unstirred suspensions by adding 5% of Na_2O into the initial mixtures were successful. Gyrolite formed 3–4 times quicker (8 h, 200 °C) in $CaO–SiO_2 \cdot nH_2O$ mixtures and in CaO–quartz mixtures during 16 h (in pure mixtures gyrolite has not formed even after the synthesis of one week) [26].

Most of chemical reactions, also calcium silicate hydrates formation becomes more intensive when the initial mixture is stirred. However, no data were found in references about the influence of stirring on gyrolite synthesis.

The purpose of this work was to determine the parameters of gyrolite hydrothermal synthesis in the stirred suspensions and to examine the influence of γ-Al_2O_3 and Na_2O additives on it.

Experimental method

In this paper the following reagents as starting materials were used: fine-grained $SiO_2 \cdot nH_2O$ (ignition losses 21.43%, specific surface area S_a = 1560 m^2/kg); NaOH solution (c = 1.04%); calcium oxide (S_a = 548 m^2/kg) which has been produced by burning calcium carbonate at 1000 °C for 6 h; γ-Al_2O_3, which has been obtained after heating up $Al(OH)_3$ for 5 h at 550 °C (S_a = 712 m^2/kg).

The molar ratios of primary mixtures were C/(S+A) = 0.66 and A/(S+A) = 0 or 0.025 (C—CaO, S—SiO_2, A—Al_2O_3). The amount of NaOH, corresponding to 5% of Na_2O from the mass of dry materials, added in the form of solution and additionally added necessary quantity of water that water/solid ratio of the suspension was equal to 10.0. Hydrothermal synthesis has been carried out in rotative autoclave (10 rpm) under the saturated steam pressure at 200 °C temperature; the duration of isothermal curing was 2, 4, 6, 8, 16, 24, 32, 48, or 72 h. The products of the synthesis have been filtrated, rinsed with ethyl alcohol to prevent carbonization of material, dried at a temperature of 100 °C ± 5, and sieved through the sieve N 005.

The X-ray powder diffraction data were collected with DRON-6 X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with 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°.

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

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

The specific surface area of the raw materials was determined by the Blaine's method.

Results and discussions

At the beginning of the reaction (2 and 4 h) in the stirred $CaO–SiO_2 \cdot nH_2O–H_2O$ mixture the formation of a semicrystalline C-S-H(I) type calcium silicate hydrate was observed (Fig. 1, curves 1, *d*-spacing—1.244; 0.305; 0.279; 0.183 nm). This compound begins to transform into Z-phase (*d*-spacing—1.556; 0.840; 0.417; 0.371; 0.306; 0.279; 0.184 nm) and gyrolite gel (*d*-spacing—2.281; 1.126; 0.837; 0.419; 0.373; 0.351; 0.280; 0.214 nm), when the duration of isothermal curing was extended till 6 hours (Fig. 1, curve 2).

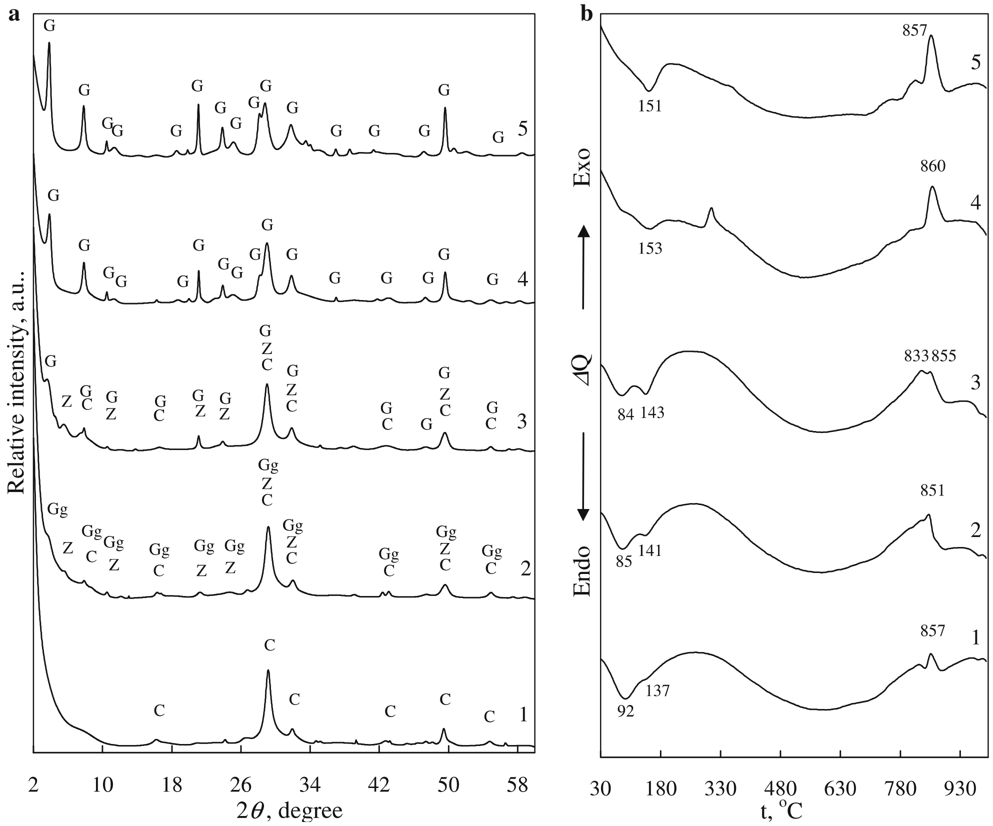


Fig. 1 X-ray diffraction patterns (**a**) and DSC curves (**b**) of synthesis products in the CaO–SiO$_2$·nH$_2$O–H$_2$O system. Duration of hydrothermal synthesis at 200 °C: 1–4 h; 2–6 h; 3–8 h; 4–16 h; 5–48 h. *Indexes:* C—C-S-H(I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite

It has been determined that low-base calcium silicate hydrates thermal behaviour is quite complex. The DSC curves exhibit two main endothermic peaks at the temperature range of 80–150 °C. The first peak occurs at 92 °C, and can be associated with the removal of physisorbed (surface) water from C-S-H(I) structure. The second broad endothermic peak at the temperature range of 137–143 °C is related to the loss of physisorbed and interlayer water from the crystal structure of the Z-phase and gyrolite (Fig. 1b, curves 1, 3). The XRD analysis confirmed the obtained DSC results: only C-S-H(I) characteristic peaks dominated in the X-ray diffraction pattern after four hours of synthesis. Meanwhile, after six hours of isothermal curing the new peaks of small intensity already can be identified which characterize the presence of small amounts of Z-phase (*d*-spacing—1.556 nm) and gyrolite gel (*d*-spacing—2.281 nm) (Fig. 1, curve 2).

The increment of main XRD peaks (*d*-spacing—1.556 and 2.281 nm) shows the larger quantities of Z-phase and gyrolite form when the synthesis is continued (8 h).

Moreover, small intensity of the exothermic effect at 833 °C temperature in DSC curve evidence that the traces of C-S-H(I) remains in the products. It should be noticed that more clear endothermic peak characterizing low-base calcium silicate hydrates was determined at the temperature of 143 °C (Fig. 1b, curve 3).

Z-phase rapidly turns into gyrolite after prolonging the duration of isothermal curing. The disappearance of the main Z-phase peak in XRD pattern confirms the end of transformation process after 16 h of synthesis (Fig. 1, curve 4). Meanwhile, Z-phase has transformed into gyrolite only after 32 h when synthesis was proceeded without stirring. It was noticed that in the unstirred suspensions Z-phase was always intermediary compound in the gyrolite synthesis [18]. These data correspond to a previous works in this field [14–16, 18].

Moreover, our research allows to state that in the stirred suspensions under favourable synthesis conditions (high temperature, active SiO$_2$ component, dispersive starting materials), gyrolite can crystallize at the same time with Z-phase. It is presumable that under the selection of more favourable conditions (higher temperature and vigorous stirring), it is possible to avoid the intermediate compounds in gyrolite synthesis.

Scanning electron microscopy (SEM) showed that the structure of gyrolite crystals depends on synthesis duration. After 16 h of synthesis particles consist of very small plate crystallites (Fig. 2a). Meanwhile, after 24 h of hydrothermal curing the plate crystal structure of gyrolite appear in the product (Fig. 2b). Recrystallization process of the plate crystal structure of gyrolite become clearer during 48 h and started to dominate (Fig. 2c). This view agrees with XRD data (Fig. 1a, curve 5).

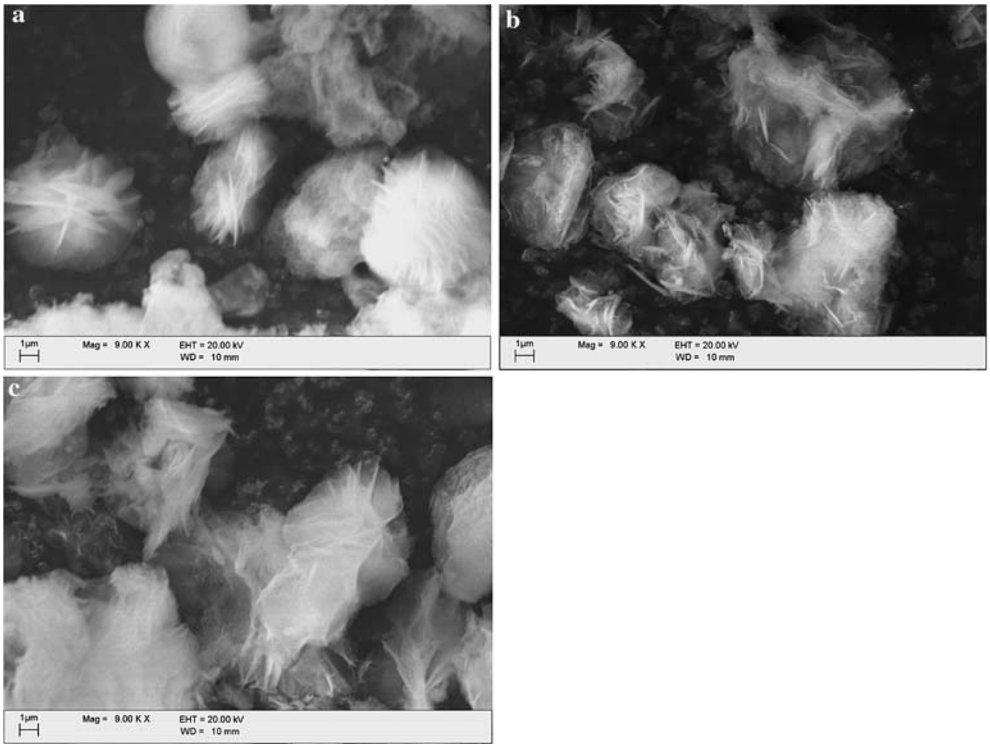
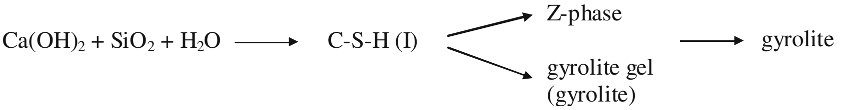


Fig. 2 Scanning electron micrographs of synthesis products in the CaO–$SiO_2 \cdot nH_2O$–H_2O system. Duration of hydrothermal curing at 200 °C: (**a**) 16 h; (**b**) 24 h; (**c**) 48 h

It is possible to assume that the reactions of new compounds formation in stirred (10 rpm) suspensions of CaO and amorphous SiO_2 at 200 °C, occur in the following sequence:



$$\begin{tikzcd} Ca(OH)_2 + SiO_2 + H_2O \arrow[r] & \text{C-S-H (I)} \arrow[r] \arrow[dr] & \text{Z-phase} & \longrightarrow \text{gyrolite} \\ & & \text{gyrolite gel (gyrolite)} & \end{tikzcd}$$

Thus, the reactions of gyrolite formation proceed two times faster in the stirred suspension and this compound already forms after 16 h of isothermal curing.

In order to synthesize gyrolite in shorter period of time, small amount of Na_2O and/or γ-Al_2O_3 were added into the initial mixtures.

By the presence of 5% Na_2O, C-S-H(I) already forms after 2 h of isothermal curing (Fig. 3, curve 1, exothermic peak at 803 °C) and $Ca(OH)_2$ do not react fully through such a short time (Fig. 3b, curve 1, endothermic peak at 502 °C). Proceeding synthesis, already after 4 h gyrolite gel and Z-phase rudiments were seen together with C-S-H(I) (Fig. 3, curve 2).

It should be underlined, that Z-phase in the mixtures with Na_2O exists approximately twice shorter than in pure mixtures, because gyrolite dominates in products after 6 h of hydrothermal curing (Fig. 3, curve 3). It can be mentioned that gyrolite in mixtures with Na_2O is metastable, because already after 16 h of isothermal curing the rudiments of new compound—pectolite are identified (Fig. 3, curve 4, *d*-spacing—0.291; 0.292; 0.308; 0.307; 0.330 nm). However, in the unstirred suspensions at the temperature of 200 °C pectolite appeared only after one week (168 h) [26]. The peaks intensities of pectolite and gyrolite in X-ray diffraction pattern grow having prolonged synthesis for 24 h but later (32, 48, 72 h) the intensity of main gyrolite basic reflection do not change (Fig. 3, curve 5). The accumulation of two morphologous crystals can be seen in SEM micrographs: gyrolite characteristic plate shape crystals and long, needle shape pectolite crystals that are formed as on gyrolite plates and in the interlayers between them (Fig. 4).

The results of EDS analysis indicates that ~1.9% of Na enter into the structure of crystal compounds after 16 h of isothermal curing. It was determined that prolonging the duration of hydrothermal treatment up to 24 and 48 h, the amount of inserted Na grows respectively ~2.5% and ~3.2% (Fig. 4d).

Thus, in the stirred suspensions, Na_2O positively affects gyrolite synthesis, but also shortens the duration of its stability.

It should be underlined that not only calcium silicate hydrates but also calcium aluminum silicate hydrates or hydrogarnets form in CaO–$SiO_2 \cdot nH_2O$–Al_2O_3–H_2O system

Fig. 3 X-ray diffraction patterns (**a**) and DSC curves (**b**) of synthesis products in the CaO–SiO_2·nH_2O–Na_2O–H_2O system. Duration of hydrothermal synthesis at 200 °C: 1–2 h; 2–4 h; 3–6 h; 4–16 h; 5–48 h. *Indexes:* C—C-S-H(I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite, I—pectolite

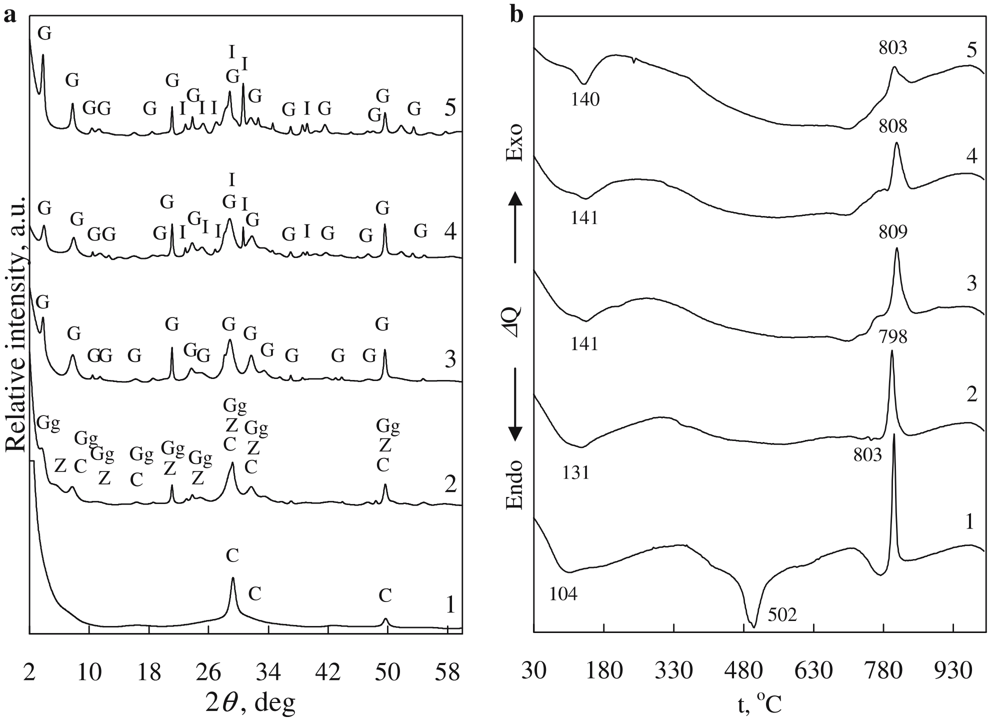
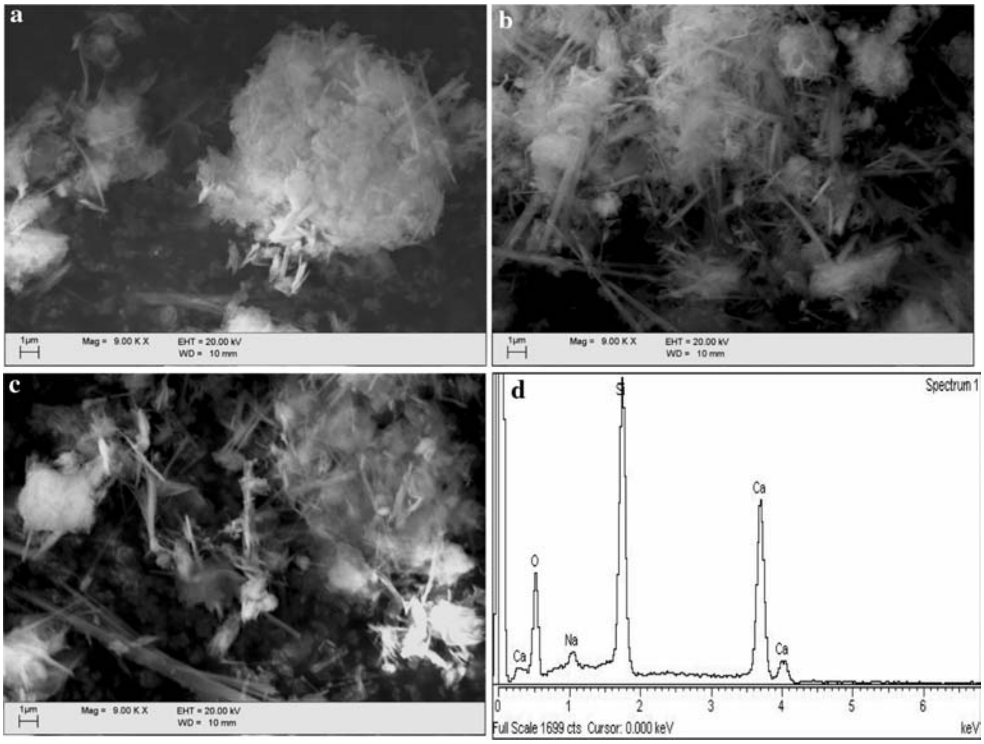


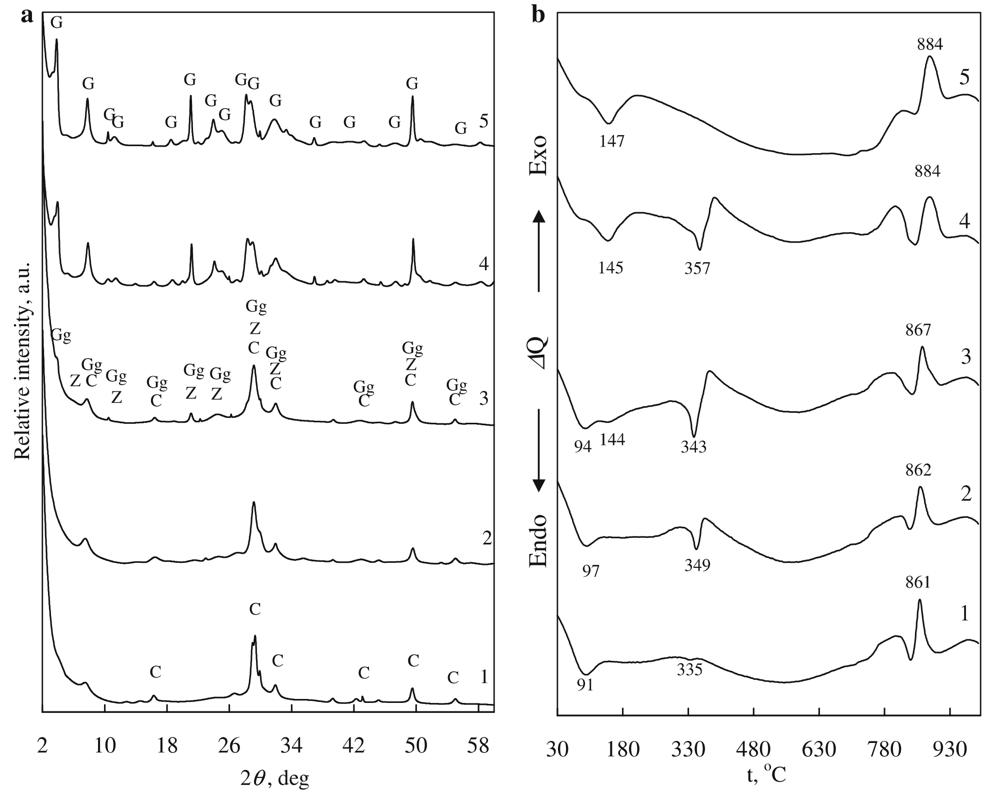
Fig. 4 Scanning electron micrographs (**a**, **b**, **c**) and EDS analysis curve (**d**) of synthesis products in the CaO–SiO_2·nH_2O–Na_2O–H_2O system. Duration of hydrothermal synthesis at 200 °C: (**a**) 16 h; (**b**) 24 h; (**c**) and (**d**) 48 h



at 200 °C (Fig. 5). Many compounds form the group of calcium aluminum silicate hydrates or hydrogarnets with almost the same interplannar distances *d*, as a result the peaks overlap. Basic reflection intensity of metioned compounds in X-ray diffraction pattern is rather small as only 2.6% Al_2O_3 was added into initial mixture; that's why it is very difficult to assign product to the particular compound (calcium aluminum silicate hydrates and hydrogarnets).

For this reason, in the further discussion those compounds would be named calcium aluminum silicate hydrates (CASH), where the number of SiO_2 moles varies from 0 to 3. DSC analysis showed that after 2 h of syn-

Fig. 5 X-ray diffraction patterns (**a**) and DSC curves (**b**) of synthesis products in the CaO–SiO$_2$·nH$_2$O–Al$_2$O$_3$–H$_2$O system. Duration of hydrothermal synthesis at 200 °C: 1–2 h; 2–4 h; 3–16 h; 4–48 h; 5–72 h. *Indexes:* C—C-S-H(I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite



thesis the CASH rudiments form together with C-S-H(I)—endothermic peak at 335 °C and exothermic peak at 861 °C were obtained respectively (Fig. 5, curve 1).

The first peak grows when the duration of hydrothermal curing is prolonged (4; 6; 8; 16 h): it means that bigger amount of CASH forms in the products (Fig. 5, curves 2, 3). We suppose that it is related to a low reactivity of γ-Al$_2$O$_3$. It shoud be noticed that CASH begin to decompose when the synthesis is prolonged up to 48 h, because the intensity of endothermic peak at 357 °C decreases (Fig. 5b, curve 4). CASH decomposes fully when the duration of synthesis is prolonged more (72 h) (Fig. 5b, curve 5). The results of EDS analysis confirmed that aluminum interferes into the structure of crystal after the long isothermal curing time.

γ-Al$_2$O$_3$ impedes the formation of low-base calcium silicates hydrates, because their rudiments are identified only after 16 h (Fig. 5, curve 3). Besides, this additive stabilizes Z-phase—its small amounts together with gyrolite were seen in all explored conditions (Fig. 5, curve 3–5).

However, when Na$_2$O is added into CaO–SiO$_2$·nH$_2$O–Al$_2$O$_3$–H$_2$O system, CASH do not form (Fig. 6, curve 1–4). It should be underlined that Na$^+$ and Al^{3+} ions positively influence Z-phase because after 4 h very intensive peak with *d*–spacing–1.5 nm can be seen in X-ray diffraction pattern (Fig. 6, curve 1).

Moreover, Z-phase remains stable for the very short period of time, because after 6 h of isothermal curing, the rudiments of gyrolite gel crystals dominate in products (Fig. 5, curve 2). The larger amount of gyrolite forms when the synthesis is proceeding (Fig. 5, curve 3–4). It was determined that the presence of Al$_2$O$_3$ additive in the CaO–SiO$_2$·nH$_2$O–Na$_2$O–H$_2$O suspension stabilizes gyrolite and prevents its transformation to pectolite.

Conclusions

1. In the CaO–SiO$_2$·nH$_2$O–H$_2$O system the reactions of low-base calcium silicate hydrates in the stirred suspensions proceed approximately twice quicker to compare with unstirred suspensions; pure gyrolite forms already after 16 h of isothermal curing at 200 °C. Stirring affects the sequence of intermediate compounds: gyrolite crystallizes together with Z-phase.
2. It was determined that the presence of 5% Na$_2$O additive in the stirred suspensions significantly accelerates the synthesis of gyrolite: this compound dominates already after 6 h at 200 °C.
3. Gyrolite is not stable in the mixture with Na$_2$O additive and begins to transform into pectolite when the synthesis is prolonged up to 16 h. The presence of Al$_2$O$_3$ additive in the CaO–SiO$_2$·nH$_2$O–Na$_2$O–H$_2$O suspension stabilizes gyrolite and prevents its transformation to pectolite.

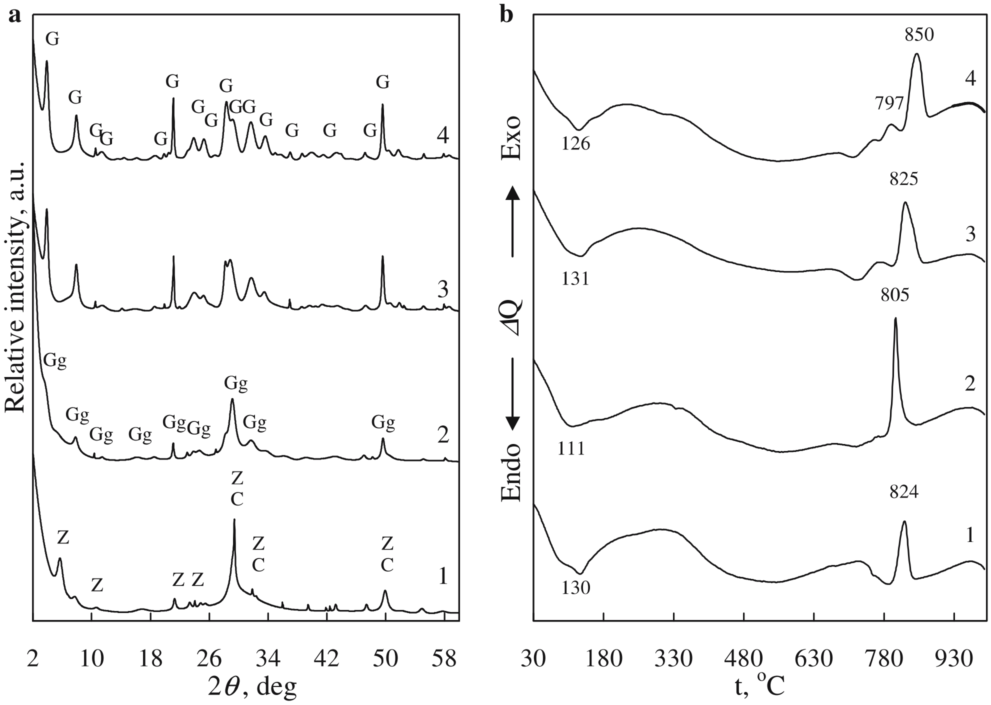


Fig. 6 X-ray diffraction patterns (**a**) and DSC curves (**b**) of synthesis products in the CaO–SiO_2·nH_2O–Na_2O–Al_2O_3–H_2O system. Duration of hydrothermal synthesis at 200 °C: 1–4 h; 2–6 h; 3–24 h; 4–72 h. *Indexes:* C—C-S-H (I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite

4. γ-Al_2O_3 additive is not recommendable for the synthesis of gyrolite, because Al^{3+} ions stimulate formation of C-S-H(I), CASH and prolongs the time of their existence.

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