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Influence of gypsum additive on the gyrolite formation process

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ABSTRACT

The influence of gypsum additive on the gyrolite formation process and a sequence of intermediary compounds formation in the $CaO–SiO_2 \cdot nH_2O–H_2O$ system was examined and explained. The synthesis has been carried out in unstirred suspensions. The molar ratios of primary mixtures were $CaO/SiO_2 = 0.66$. The amount of sulphate ions to be added to a raw mixture was 1–10%. The duration of isothermal curing at 200 °C was 4, 8, 16 and 72 h.

It was determined that the quantity of sulphur which penetrates into the crystalline structure of gyrolite depends not only on the synthesis conditions but also on the composition of initial mixture. A larger amount of sulphate ions stimulate the formation not only of gyrolite, but also of $CaSO_4$. Gypsum additive has no influence on the re-crystallization temperature of C–S–H(I), Z-phase and gyrolite into wollastonite. The composition of initial mixtures is recommended to calculate according to molar ratios. In other cases, upon increasing the amount of sulphate ions, the basicity of the mixture decreases and gyrolite forms more difficult.

1. Introduction

Calcium silicate hydrates can be produced either by air curing, e.g. like in cement or concrete, or hydrothermally by high pressure steam curing in an autoclave. The production processes for fibre cement, calcium silicate boards and autoclaved aerated concrete cover the whole range of calcium silicate hydrates from poorly crystallized and semi crystallized to well crystallized. The type of curing, and consequently the type of calcium silicate hydrate produced, have a significant effect on the properties of the building material [1–11].

The reaction pathway of calcium silicate hydrates is governed by various parameters such as temperature, stirring, the presence of foreign ions and their concentrations, which influence the kinetics of the reaction and even the microstructure of the products. The effectiveness of each additive depends on the properties of raw materials, the parameters of the hydrothermal synthesis and other factors. Published articles describe the influence of alkaline metals [12–18], aluminium [19–28] and of other elements [29–36] on the synthesis and properties of calcium silicate hydrates.

There are many external sources of sulphate, including industrial waste waters and solid waste exposed to ground or surface water. It can also be found naturally in the clinker itself. These levels of sulphate are not usually high enough to cause any expansion. Less often, sulfate can be found in the aggregate in the form of gypsum or pyrite, in mixing water, and in admixtures such as fly ash [37]. Moreover, large quantities of the by-product, gypsum, are produced by chemical industries and are currently being disposed of by dumping into rivers, ponds or landfills. Due to increasing concerns about environmental pollution, it is essential to utilize these wastes as building material. For these reasons, the study of the influence of gypsum additives on the synthesis of calcium silicate hydrates is very important and actual [38–49].

S. A. Krzheminskij et al. [39,40] indicated that at 175 °C when the molar ratio of the primary mixture is $CaO/SiO_2 = 0.5–1.0$, small amounts (1–5%) of sulphate ions stimulate the reaction of CaO with C–S–H(I). As the final products of such synthesis, 1.13 nm tobermorite and xonotlite are formed.

K. K. Kuatbaev [44] has proven that small amounts of gypsum additive also have a positive effect on the crystallization of calcium silicate hydrates. Meanwhile, in mixtures with a higher content (15–35%) of this additive, together with calcium silicate hydrates ellastadite is also formed. K. K. Kuatbaev has shown that gypsum additive has no influence on the solubility of quartz, but he stated that gypsum is more soluble than quartz and the solution contains a significant excess of anions. For this reason, SiO_4^{4-} is isomorphically replaced by SO_4^{2-}, and SO_3-substituted calcium silicate hydrates, more soluble than pure compounds, are formed.

S. I. Grabko [45] has determined that in mixtures with a molar ratio $CaO/SiO_2 = 0.8$, gypsum additive primarily significantly stimulates the formation of ellastadite. The author indicates that calcium silicate hydrates start forming when all the volume of $CaSO_4$ has reacted. In this case, in the products α-C_2S hydrate prevails and during synthesis gradually recrystallizes into SO_3-substituted C–S–H(I) while in the pure system only C–S–H(I) is formed. S. I. Grabko has determined that

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even 7% of sulphate ions can enter into the crystal structure of these compounds. However, using a larger quantity of this additive, C–S–H (I) is metastable and regroups into 1.13 nm tobermorite.

R. Vektaris et al. [46,47] have also determined that sulphate ions stimulate formation of calcium silicate hydrates. Upon increasing the amount of gypsum in the CaO–quartz–H_2O mixture, it was noticed that the solubility of $Ca(OH)_2$ decreased and at the same time the crystallization of calcium silicate hydrates occurred faster. This process proceeds more intensively in mixtures with a molar ratio $CaO/SiO_2=0.8$ than in mixtures with a molar ratio $CaO/SiO_2=1.0$. Moreover, in the CaO–amorphous-SiO_2–H_2O system, 5–10% of gypsum additive strongly effects the crystallization of C–S–H(I) into 1.13 nm tobermorite.

P. P. Budnikov, L. A. Krojchuk and B. H. Vinogradov [41,48,49] indicated that in lime–quartz–water mixtures under hydrothermal conditions at 175 °C sulphate ions have no influence on the solubility of lime, but affects the mineral composition of the final products: at the beginning of the synthesis dominate C–S–H(II) and α-C_2S hydrate which prolonging the duration of synthesis transform into C–S–H(I), 1.13 nm tobermorite and xonotlite.

On the other hand, I. A.Veretinskaja, M. Sakiyama and T. Mitsuda [42,43] supposed that a small amount (2.5%) of gypsum additive reduces the formation rate of calcium silicate hydrates in the CaO–SiO_2–H_2O system. It was determined that this rate decreases in mixtures with a molar ratio $CaO/SiO_2=1.0$ and water/solid = 3. Meanwhile, larger quantities of gypsum additive have no influence on the sequence of compounds formation. Besides, it was estimated that only 1.5% of sulphate ions can enter into the calcium silicate hydrate crystal structure. P. P. Budnikov, L. A. Krojchuk and B. H. Vinogradov [41,49] have also found out that sulphate ions have a negative influence on the formation of calcium silicate hydrate in lime–quartz mixtures with a molar ratio $CaO/SiO_2=0.8$, water/solid = 20 at 175 °C.

It has been commonly known that the formation of gyrolite proceeds via disordered intermediate phases. In gyrolite synthesis, the initial C–S–H gel transforms to Z-phase and then finally recrystallizes to gyrolite. The influence of alkaline metals, aluminium and other elements on C–S–H(I) transformation into gyrolite has been explored by only a few authors [29,50–54]. Meanwhile, no data have been published and it is completely unknown whether the sulphate ions can alter the formation and crystal structure of gyrolite or Z-phase.

The main objective of the present work was to examine the influence of sulphate ions on the gyrolite formation process in the CaO–$SiO_2\cdot nH_2O$–H_2O mixture as well as to analyze and explain the sequence of intermediary compound formation.

2. Materials and methods

In this work, the following reagents were used as starting materials: fine-grained $SiO_2\cdot nH_2O$ (losses on ignition 21.43%, specific surface area $S_a=1560$ m²/kg); calcium oxide ($S_a=548$ m²/kg); $CaSO_4\cdot 2H_2O$ (losses on ignition 23.05%).

The amount of the additive to be added to a raw mixture was calculated by two methods. The first method is based on the assumption, that the equivalent amount of Si^{4+} is isomorphically replaced by S^{6+}. Therefore, the composition of initial mixtures was calculated according to the molar ratios: $CaO/(SiO_2+SO_3)=0.66$ and $SO_3/(SiO_2+SO_3)=0$; 0.0125; 0.025; 0.05; 0.1 and 0.125. The second method was built on the assumption that the Si^{4+} is only partly replaced by S^{6+}, and the other part of the latter ions enter into the interlayers of the products. In this case, by increasing the amount of sulphate ions from 2 to 10%, the molar CaO/SiO_2 ratio decreases from 0.66 to 0.58.

Dry primary mixtures were mixed with water to reach the water/solid ratio of the suspension equal to 10.0. Hydrothermal synthesis was carried out under the saturated steam pressure at a temperature of 200 ºC; the duration of isothermal curing was 4, 8, 16 and 72 h. The products of the synthesis were filtered, rinsed with ethyl alcohol to prevent carbonization, dried at a temperature of 50 ºC ± 5, and sieved through a sieve with a mesh size of 80 µm.

The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with the Bragg–Brentano geometry using Ni-filtered Cu K_α radiation and 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 $2\theta=0.02°$. To describe the diffractional background under the 3rd degree Tchebyshev polynom, we have used fundamental parameters peak profiling (a computer program X-fit) [55].

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

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

Scanning electron microscopy (SEM) (Oxford ISIS Leo 440 i) coupled with energy dispersive X-ray spectrometer (EDS) was performed using an 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 Blaine's method with an air permeability apparatus (Model 7201, Toni Technik Baustoffprufsysteme GmbH).

3. Results and discussion

It was determined that in unstirred CaO–$SiO_2\cdot nH_2O$–H_2O suspension at the beginning of the reaction gypsum additive affects the sequence of calcium silicate hydrates formation. In pure mixture after 4 h of isothermal curing, only the traces of Z-phase (Fig. 1, curves 1, *d*-spacing—1.554; 0.823; 0.418; 0.305; 0.279 and 0.183 nm) together with C–S–H(I) were formed (Fig. 1, curve 1, *d*-spacing—0.306; 0.279 and 0.184 nm). Meanwhile, a small amount of sulphate ions (the molar ratio $SO_3/(SiO_2+SO_3)=0.0125$), stimulates the formation of Z-phase because as soon as within 4 h in XRD curve a very intensive diffraction peak with *d*-spacing—1.553 nm was identified (Fig. 1, curve 2). This fact indicates that sulphate ions accelerate the formation of intermediary compound in the gyrolite synthesis. It should be underlined that C–S–H(I) and Z-phase are unstable because within 8 h of isothermal curing in the products the rudiments of gyrolite gel (*d*-spacing—2.356; 1.103; 0.840; 0.420; 0.306; 0.281 and 0.183 nm) were already identified (Fig. 1, curve 3). These results correspond to the reference data [53,54] and show that while synthesizing gyrolite, the Z-phase serves as an intermediary compound. Moreover, within 16 and 72 h of hydrothermal treatment, the same compounds as in the synthesis without using gypsum additive – Z-phase, gyrolite gel and gyrolite – are formed (Fig. 1, curves 4–6).

Thus, a small amount of sulphate ions in the initial mixture stimulates Z-phase formation and enters into the crystal structure of gyrolite.

A larger amount of sulphate ions (the molar ratio $SO_3/(SiO_2+SO_3)=0.025$), accelerates the formation of Z-phase together with C–S–H(I) because after 4 h of synthesis in XRD curve a very intensive diffraction peak with *d*-spacing—1.553 nm was identified (Fig. 2, curve 1). Moreover, in the products, together with the mentioned compounds, $CaSO_4$ (*d*-spacing—0.350; 0.285 nm) was noted. This fact confirmed that calcium sulphate has a very low

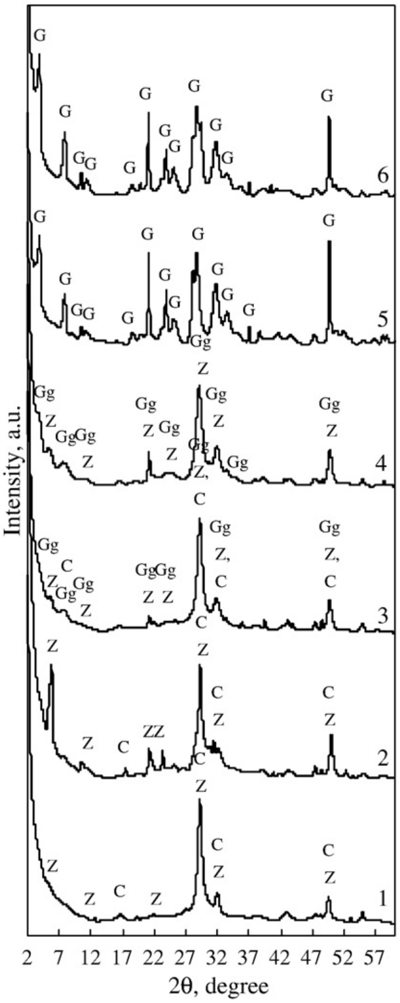

Fig. 1. X-ray diffraction patterns of synthesis products when the composition of the primary mixture given in molar ratios is equal to $CaO/(SiO_2+SO_3)=0.66$ and $SO_3/(SiO_2+SO_3)=0$ and 0.0125. Duration of hydrothermal synthesis at 200 °C: 1–4 h, pure mixture; 2–4 h, with gypsum additive; 3–8 h, with gypsum additive; 4–16 h, with gypsum additive; 5–72 h, with gypsum additive; 6–72 h, pure mixture. *Indexes:* C—C–S–H(I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite.

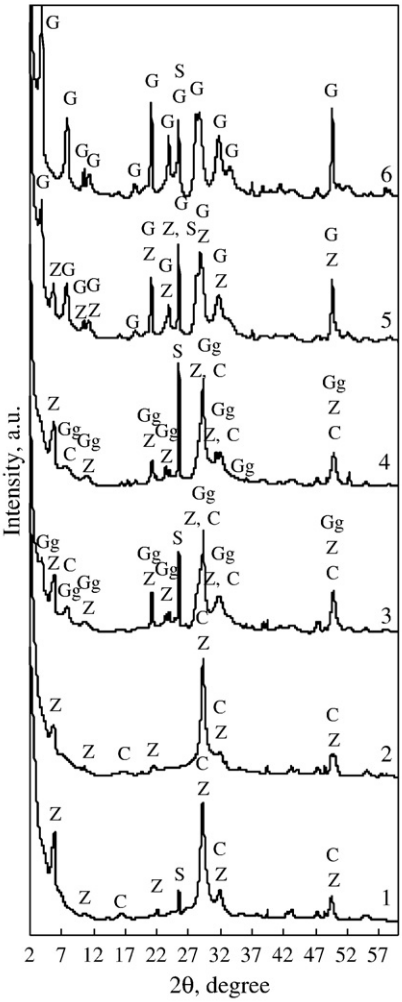

Fig. 2. X-ray diffraction patterns of synthesis products when the composition of the primary mixture given in molar ratios is equal to $CaO/(SiO_2+SO_3)=0.66$ and $SO_3/(SiO_2+SO_3)=0.025$ (curves 1, 3, 5, 6) and upon adding 2% of SO_3 ions of dry substance mass (curves 2, 4). Duration of hydrothermal synthesis at 200 °C: 1, 2–4 h, 3, 4–8 h, 5–16 h, 6–72 h. *Indexes:* C—C–S–H(I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite, S—$CaSO_4$.

solubility (at 20 °C the solubility is 0.2 g/100 g H_2O) which decreases with increasing the temperature. In this case, the initial mixture contained 44% of excess of sulphur according to $CaSO_4$ solubility. The results of EDS analysis indicates the fact that sulphur incorporates into structure of calcium silicate hydrates. In our experimental conditions after 4 h of isothermal curing EDS data show that ~0.26 wt.% of S (31% of the initial amount of sulphur) enters into the structure of crystal compounds (Fig. 3b). Thus, 13% $CaSO_4$ remained insoluble which is visible in XRD curve (Fig. 2, curve 1). However, the data of SEM analysis presented only aggregates of plate shape crystals characteristic to Z-phase (Fig. 3a).

During the synthesis by using a second method of calculating the quantity of gypsum additive and upon adding 2% of SO_3 ions of the dry substance mass (which corresponds to the same amount as that of $SO_3/(SiO_2+SO_3)=0.025$) to the mixture, unexpected results were obtained: the XRD curve showed that the intensity of the Z-phase peak was 3–4 times lower compared to the data obtained when the mixture was prepared according to the molar ratios (Fig. 2, curve 2). Interestingly, all additive was incorporated into the crystal structure of these compounds as in the mixtures, calculating according to molar ratios, the rudiments of $CaSO_4$ have been already formed (Fig. 2, curve 1).

By using a mixture with 2% of gypsum additive, only after 8 h of hydrothermal treatment Z-phase and $CaSO_4$ prevail in the products (Fig. 2, curve 4). Besides, in the mixture prepared according to molar ratios as quite a large amount of the Z-phase still remained but the gyrolite gel and calcium sulphate were already formed (Fig. 2, curve 3). After 16 h of isothermal curing at 200 °C gyrolite starts forming together with Z-phase and calcium sulphate in both mixtures (the intensity of the diffraction peak with *d*-spacing—2.345 nm increases) (Fig. 2, curve 5).

Obtained results allow us to state that at the beginning of synthesis all sulphate ions penetrate into the crystal structure of semi-crystalline calcium silicate hydrates. Later on, these compounds re-crystallize into calcium silicate hydrates in more ordered structure. During this process the part of sulphate ions extrudes into solution which react with Ca^{2+} ions and form $CaSO_4$. This phenomenon was proved by results of SEM/EDS analysis. The accumulation of two morphologies crystals can be seen in SEM micrographs: gyrolite/Z-phase characteristic plate shape crystals and long, leaf-like shape $CaSO_4$ crystals that are formed as on plates crystals and in the interlayers between them (Fig. 4a). The results of EDS analysis showed that crystals of plate structure contain only a traces (0.04 wt.%) of sulphur contrarily to leaf-like crystals ~20.55 wt.% of S (Fig. 4b).

It should be underlined that upon prolonging the synthesis an additional amount of sulphate ions starts penetrate into the

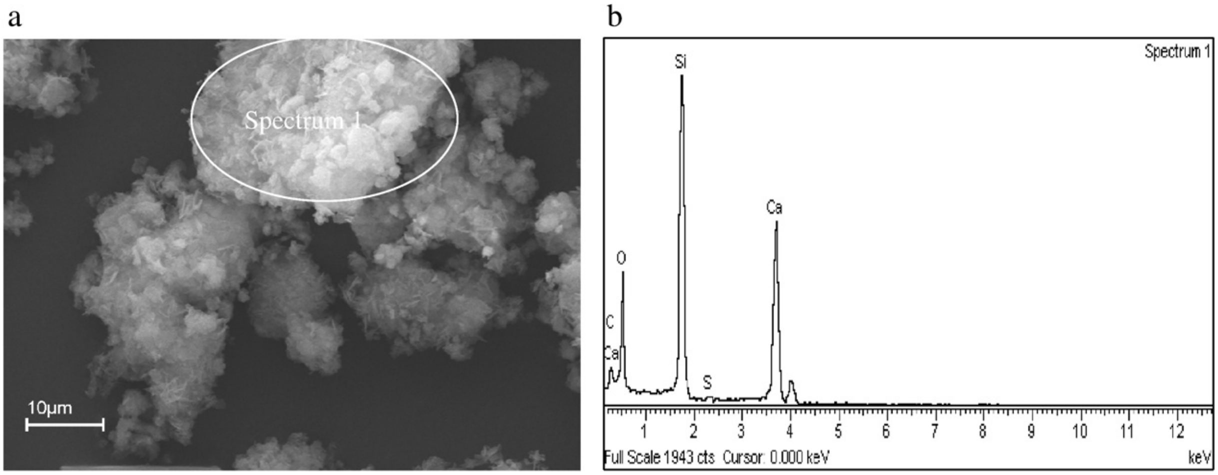

Fig. 3. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture given in molar ratios is equal to CaO/(SiO_2+SO_3) = 0.66 and SO_3/(SiO_2+SO_3) = 0.025. Duration of hydrothermal synthesis at 200 °C is equal to 4 h. Chemical composition of spectrum 1, wt.%: O — 54.50, Si — 23.90, S — 0.26, Ca — 21.35.

crystalline structure of gyrolite. It was observed that 0.1 wt.% of sulphur enters into the crystal structure of gyrolite after 72 h of isothermal curing (Fig. 5). The rest quantity of sulphur is in $CaSO_4$.

Thus, the persistence of the intermediate compounds (i.e. the beginning of formation and the end of transformation into other compounds) in gyrolite synthesis depends not only on synthesis conditions but also on the method of calculating the amount of additive to be added to a raw mixture.

It was determined absence of any significant changes in the sequence of compounds formed at 200 °C when the amount of sulphate ions was increased (SO_3/(SiO_2+SO_3) = 0.05 or 0.1) in the mixture. The XRD data indicate that a well-crystallized Z-phase, C–S–H(I) and calcium sulphate forms in the products after 4 h of synthesis. The obtained FT-IR data show that in the δ(O—SiO—) range of vibrations, the Z-phase is characteristic of an intensive absorption band with the maximum in the frequency range of 461 cm^{-1} (Fig. 6b, curve 1). Moreover, in the δ(Si—O—Si) range of vibrations, the Z-phase is characteristic of low intensity bands (599 and 784 cm^{-1}). In the range of 1035 cm^{-1}, the IR spectrum of Z-phase shows an intensive peak and in 1128 cm^{-1} only a “shoulder”. In the range of symmetric vibrations of OH groups, the Z-phase spectrum indicates a wide band in the frequency range of 3463 cm^{-1}. This means that the positions of OH groups in the structure of this compound are not so well arranged compared to other calcium silicate hydrates.

It is determined that the character of the exothermic effect of a low-base calcium silicate hydrates re-crystallization into wollastonite changes. C–S–H(I) is characteristic of a narrow, sharp peak. However, when the Z-phase forms together with this compound, the exothermic effect at a temperature of ~858 °C becomes wider and more uneven as well as moves towards a higher temperature (Fig. 6a, curve 1).

After 8 h of synthesis, data of FT-IR analysis show formation of gyrolite gel, Z-phase and $CaSO_4$ (Fig. 6b, curve 2): a doublet near ~596 and ~612 cm^{-1} due to Si–O–Si bending vibrations becomes more intensive. Slightly more varied are vibrations of the 670 ... 790 cm^{-1} frequency: gyrolite has only two bands at 674 and 784 cm^{-1}. A sharp peak near 3634 cm^{-1}, which is visible only in the gyrolite spectrum, is missing in the IR spectra of all the other calcium silicate hydrates. This clear band (3634 cm^{-1}) proves that clearly distinguished OH positions exist in the structure of gyrolite, which are connected only with Ca atoms and are not influenced by hydrogen bridge links.

The XRD findings show that upon extending the duration of synthesis (16 h), the Z-phase starts regrouping into gyrolite. In addition, analysis of FT-IR and DSC data indicates the absorption

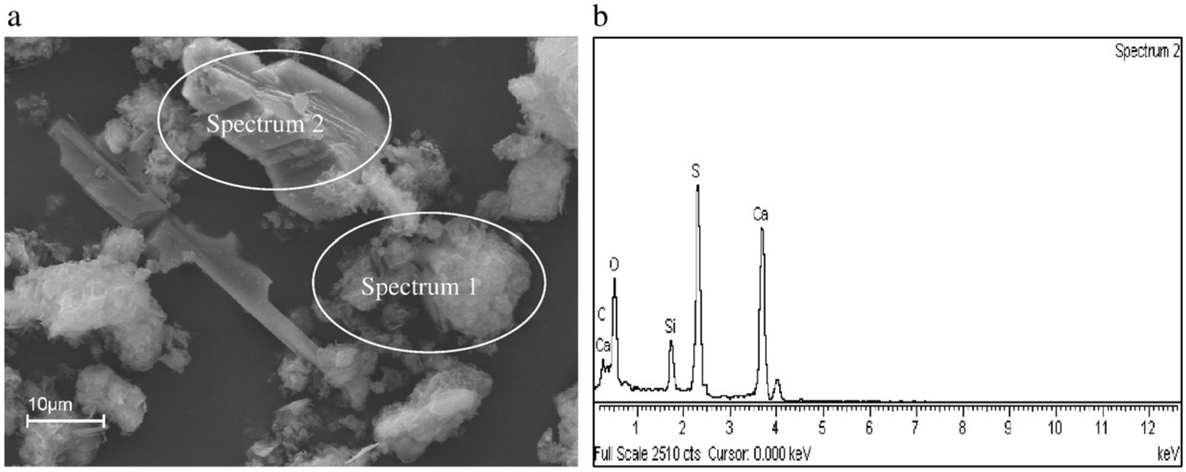

Fig. 4. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture given in molar ratios is equal to CaO/(SiO_2+SO_3) = 0.66 and SO_3/(SiO_2+SO_3) = 0.025. Duration of hydrothermal synthesis at 200 °C is equal to 16 h. Chemical composition of spectrum 1, wt.%: O — 58.66, Si — 22.22, S — 0.04, Ca — 19.08; and spectrum 2, wt.%: O — 50.52, Si — 3.66, S — 20.55, Ca — 25.27.

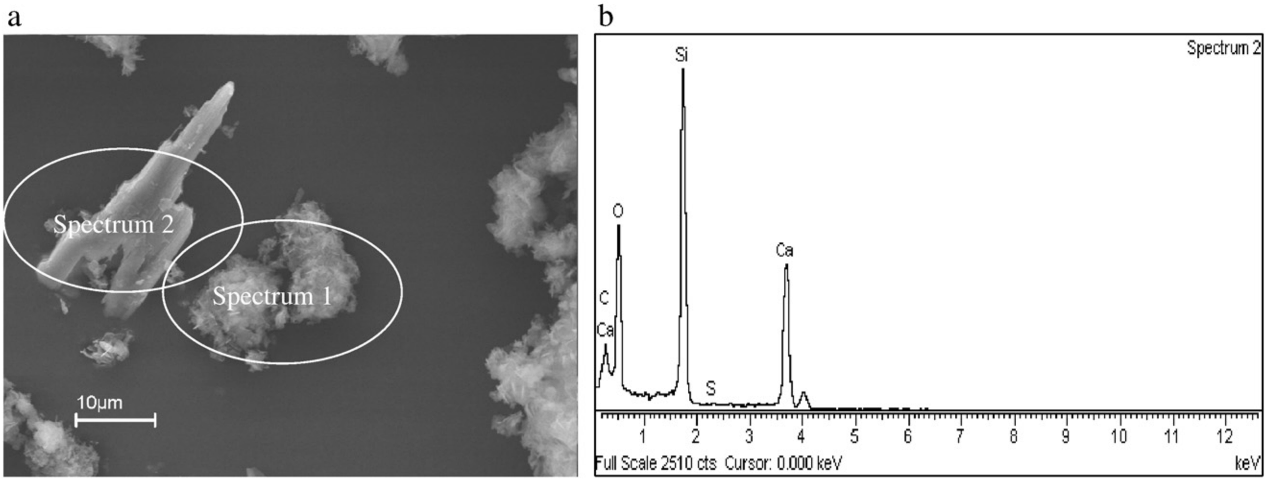

Fig. 5. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture given in molar ratios is equal to CaO/(SiO_2+SO_3) = 0.66 and SO_3/(SiO_2+SO_3) = 0.025. Duration of hydrothermal synthesis at 200 °C is equal to 72 h. Chemical composition of spectrum 1, wt.%: O — 58.71, Si — 22.15, S — 0.10, Ca — 19.05; and spectrum 2, wt.%: O — 38.11, Si — 4.00, S — 20.88, Ca — 37.01.

bands (3639, 1134 cm^{-1}) and thermal transformations (the endothermic effect at 149 °C and the exothermic effect at 857 °C) of a higher intensity (Fig. 6, curve 3). After 72 h of synthesis, like in mixtures with a smaller amount of sulphate ions, gyrolite and calcium sulphate prevailed. These results were confirmed by the data of SEM analysis: gyrolite and calcium sulphate crystals dominated in the products (Fig. 7). The results of EDS analysis indicate that ~0.35% of S enters into the structure of gyrolite (Fig. 7b).

With the aim to find out whether the persistence of intermediate compounds is different in the synthesis of gyrolite when a

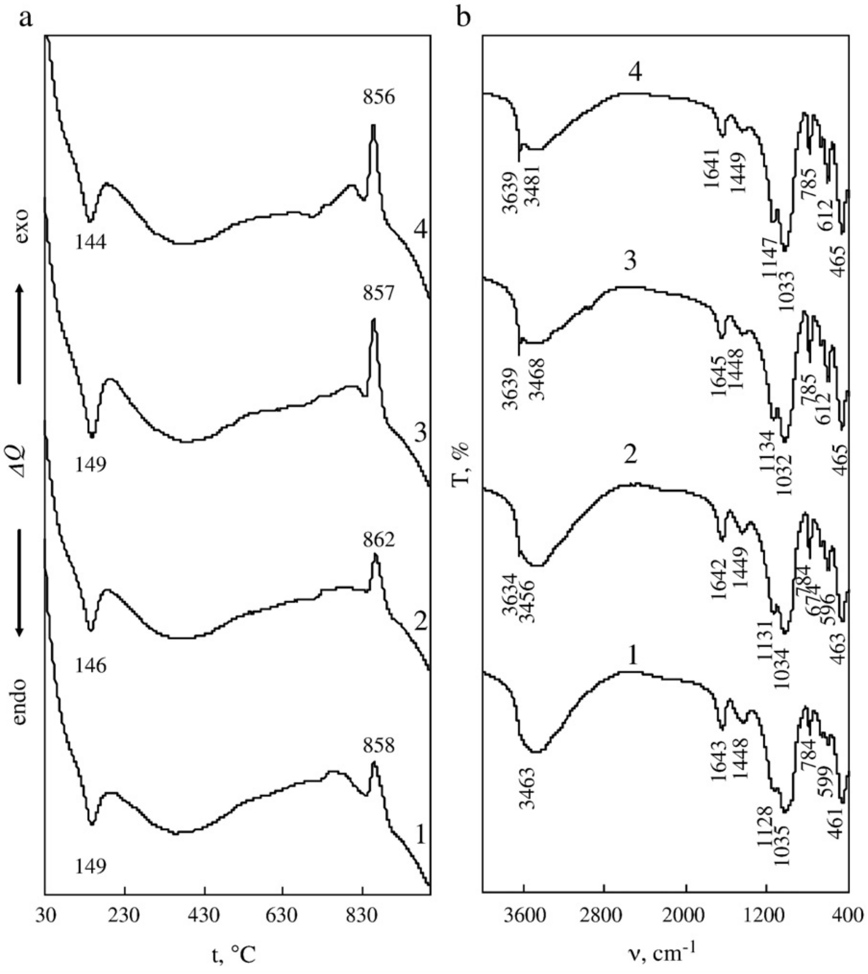

Fig. 6. DSC curves (a) and FT-IR spectra (b) of synthesis products when the composition of the primary mixture given in molar ratios is equal to CaO/(SiO_2+SO_3) = 0.66 and SO_3/(SiO_2+SO_3) = 0.05. Duration of hydrothermal synthesis at 200 °C: 1 — 4, 2 — 8, 3 — 16, 4 — 72.

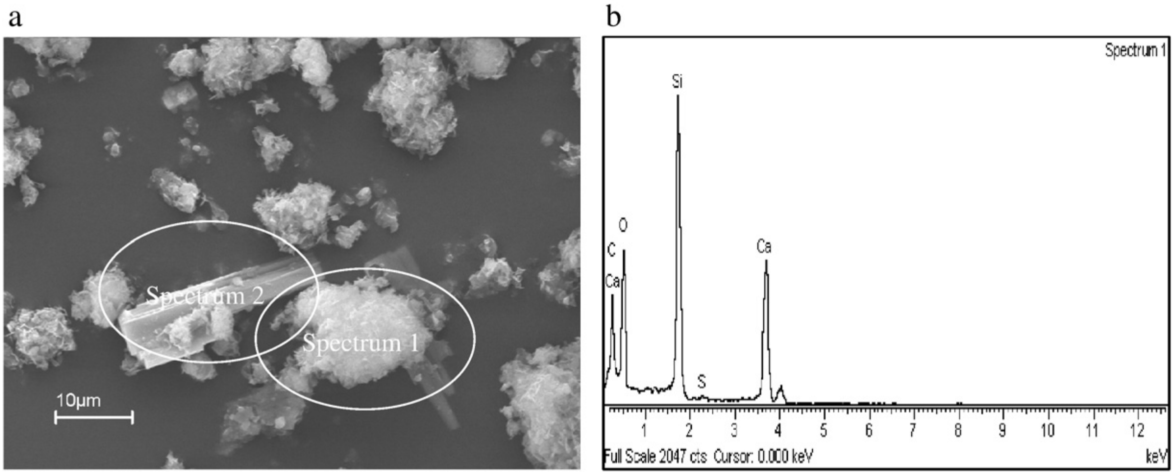

Fig. 7. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture given in molar ratios is equal to CaO/(SiO_2+SO_3) = 0.66 and SO_3/(SiO_2+SO_3) = 0.1. Duration of hydrothermal synthesis at 200 °C is equal to 72 h. Chemical composition of spectrum 1, wt.%: O — 60.18, Si — 20.25, S — 0.35, Ca — 19.22; and spectrum 2, wt.%: O — 48.16, Si — 2.32, S — 20.89, Ca — 28.63.

much bigger amount of sulphate ions of the dry substance mass is added to the mixture of raw materials, an analogous synthesis with 10% of SO_3 additive and with the mixtures having the molar ratio of SO_3/(SiO_2+SO_3) = 0.125 were carried out.

Curves of the X-ray diffraction analysis of the synthesized compounds show that after 4 h of hydrothermal exposure, similar amounts of Z-phase and calcium sulphate formed irrespective of the methods employed to calculate the mixture composition, because the intensities of the main diffraction peaks typical of them are analogous (Fig. 8, curve 1).

Another observation is that the Z-phase more rapidly regroups into gyrolite in the mixtures whose composition was also calculated according to molar ratios. Only in this case, gyrolite is also identified in the products of synthesis after 16 h (Fig. 8a, curve 3). DSC curve showed two thermal transformations typical of gyrolite (Fig. 9a, curve 1). The FT-IR spectrum also presents absorption bands characteristic of this compound (Fig. 9b, curve 1). The findings indicate that upon extending the duration of synthesis (72 h), gyrolite of a higher degree of crystallinity forms in the products. This is testified by a higher intensity of the diffraction peak with *d*-spacing—

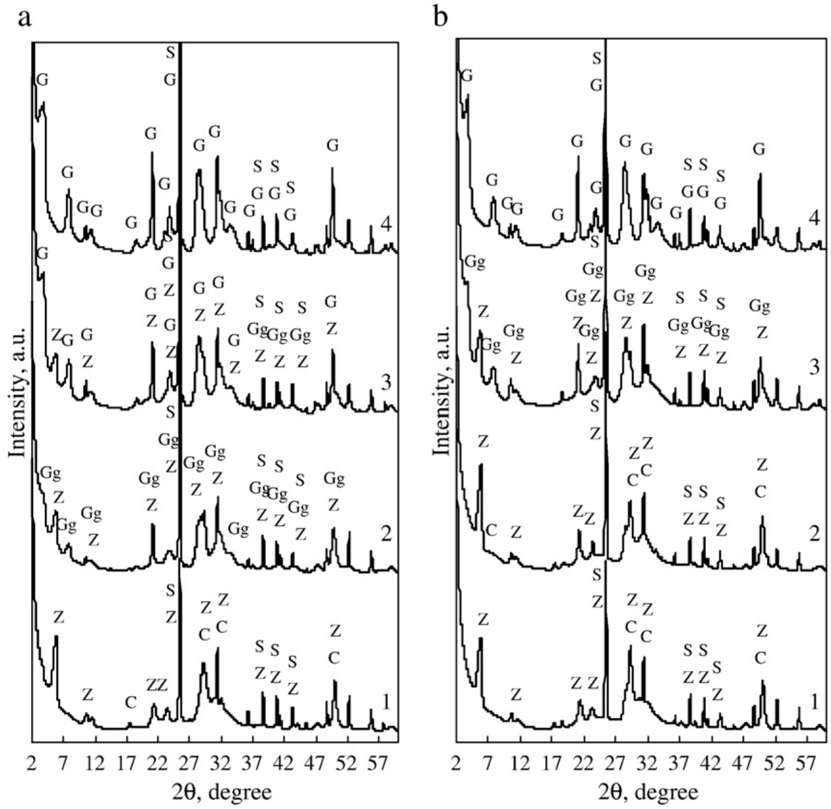

Fig. 8. X-ray diffraction patterns of synthesis products when the composition of the primary mixture given in molar ratios is equal to CaO/(SiO_2+SO_3) = 0.66 and SO_3/(SiO_2+SO_3) = 0.125 (a) and upon adding 10% of SO_3 ions of dry substance mass (b). Duration of hydrothermal synthesis at 200 °C: 1 — 4, 2 — 8, 3 — 16, 4 — 72. *Indexes:* C—C–S–H(I), Z—Z-phase, Gg—gyrolite gel, G—gyrolite, S—$CaSO_4$.

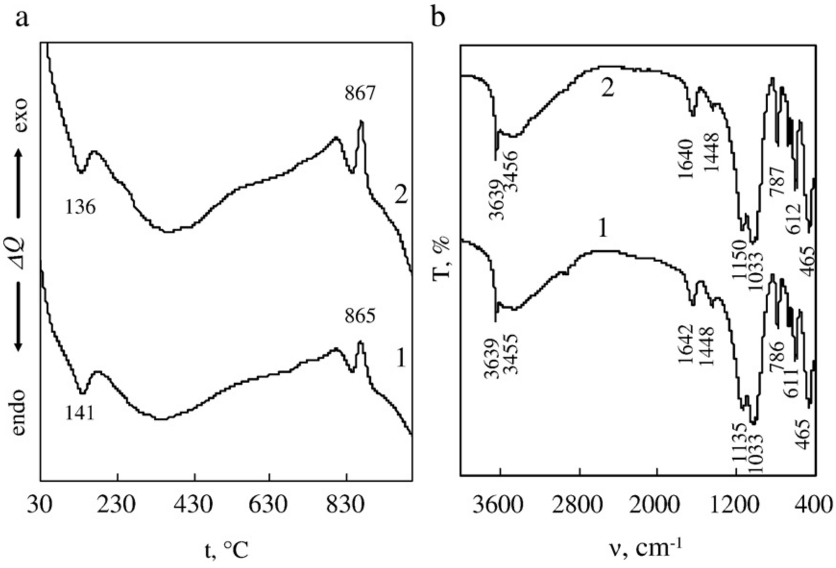

Fig. 9. DSC curves (a) and FT-IR spectra (b) of synthesis products when the composition of the primary mixture given in molar ratios is equal to $CaO/(SiO_2+SO_3)=0.66$ and $SO_3/(SiO_2+SO_3)=0.125$. Duration of hydrothermal synthesis at 200 °C: 1–16, 2–72.

2.388 nm in the XRD curve (Fig. 8a), a clearer absorption band in the range of 3639 cm^{-1} frequency in the FT-IR curve, and the exothermic effect at a temperature of 867 °C in the DSC curve (Fig. 9, curve 2).

It should be noted that in a mixture containing 10% of SO_3 ions of the dry substance mass, the transformation of Z-phase into gyrolite is more difficult: even after 8 h of isothermal curing, only Z-phase and calcium sulphate were formed (Fig. 8b, curve 2). Traces of gyrolite gel were identified after 16 h of synthesis, while after 72 h gyrolite together with $CaSO_4$ were dominated in the products (Fig. 8b, curves 3, 4).

It should be underlined that in all cases in the mixtures prepared according to the molar ratios, the typical peaks of gyrolite is more intensive than in the mixtures calculated on the mass of dry substances. It could be explained by the variation of CaO/SiO_2 ratio of initial mixture because with increasing the amount of sulphate ions from 2 to 10%, the basicity of the mixture decreases from 0.66 to 0.58 and differs from stoichiometric composition of gyrolite.

It is possible to assume that when curing the mixture of CaO, amorphous SiO_2 and $CaSO_4$ at 200 °C temperature under the saturated steam pressure, the reactions of gyrolite formation occur in the following sequence:

$$\begin{aligned}&2Ca(OH)_2+3SiO_2\cdot nH_2O+XCaSO_4\\&\quad+nH_2O\rightarrow CaO\cdot 2SiO_2\cdot nH_2O\cdot mCaSO_4\cdot pH_2O(Z{-}phase+C{-}S{-}H(I))\\&\quad+(X-m)CaSO_4\rightarrow 2Ca(OH)_2\cdot 3SiO_2\cdot nH_2O\cdot kCaSO_4\cdot pH_2O(gyrolite)\\&\quad+(X-k)CaSO_4\end{aligned}$$

The quantity of sulphate ions which enter into the crystal structure of gyrolite depends on the synthesis conditions. During the re-crystallization process of semi-crystalline calcium silicate hydrates into gyrolite, the part of sulphate ions extrudes into solution which react with Ca^{2+} ions and form $CaSO_4$. It should be noted that upon prolonging the duration of synthesis an additional amount of sulphur penetrates into the structure of gyrolite.

4. Conclusions

1. Sulphate ions at the beginning of synthesis stimulates Z-phase formation in a low-base mixture ($CaO/SiO_2=0.66$). Meanwhile, within 72 h of hydrothermal treatment, gyrolite is a final product in both mixtures: with sulphate ions as well as without them.
2. The persistence of intermediate compounds in the synthesis of gyrolite depends on the methods of calculating the gypsum additive. It is recommended to calculate the initial mixture composition according to molar ratios because crystallization process of gyrolite is more intensive.
3. It was determined that the quantity of sulphur which penetrates into the crystalline structure of gyrolite depends not only on the synthesis conditions but also on the composition of initial mixture, i.e. increasing the quantity of sulphate ions in the mixture, the amount of inserted S in gyrolite structure grows and the rest part of sulphur remains in $CaSO_4$.
4. Gypsum additive has no influence on the re-crystallization temperature of C–S–H(I), Z-phase and gyrolite into wollastonite.

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References

[1] T. Dietz, K. Bohnemann, Calcium silicate hydrate in fiber cement sheets and autoclaved aerated concrete (AAC), 7th International Inorganic-Bonded Wood & Fiber Composite materials Conference, Sun Valley, Idaho, USA, 2000, pp. 25–27.
[2] H.F.W. Taylor, D.M. Roy, Structure and composition of hydrates, Principal Report, Sub-Theme II-2, Proc. 7th Int. Cong. Chem. Cem., Paris, I, Editions Septima, Paris, 1980, II-2/1-II-2/13.
[3] X. Zhang, W. Chang, T. Zhang, C.K. Ong, Nanostructure of calcium silicate hydrate gels in cement paste, J. Am. Ceram. Soc. 83 (10) (2000) 2600–2604.
[4] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack. I. Ordinary Portland cement paste, Cem. Concr. Res. 22 (6) (1992) 1027–1038.
[5] A. Hamilton, C. Hall, Physicochemical characterization of a hydrated calcium silicate board material, J. Build. Phys. 29 (2005) 9–19.
[6] H.F.W. Taylor, Nanostructure of C–S–H: current status, Adv. Cem. Based Mater. 1 (1993) 38–46.
[7] I.G. Richardson, The calcium silicate hydrates, Cem. Concr. Res. 38 (2) (2008) 137–158.
[8] A. Nonat, The structure and stoichiometry of C–S–H, Cem. Concr. Res. 34 (2004) 1521–1528.
[9] J.J. Chen, J.J. Thomas, H.F.W. Taylor, H.M. Jennings, Solubility and structure of calcium silicate hydrate, Cem. Concr. Res. 34 (2004) 1499–1519.
[10] K. Garbev, P. Stemmermann, L. Black, C. Breen, J. Yarwood, B. Gasharova, Structural features of C–S–H(I) and its Carbonation in air — a Raman spectroscopic study. Part I: Fresh phases, J. Am. Ceram. Soc. 90 (2007) 900–907.

[11] L. Black, K. Garbev, G. Beuchle, P. Stemmermann, D. Schild, X-ray photoelectron spectroscopic investigation of nanocrystalline calcium silicate hydrates synthesised by reactive milling, Cem. Concr. Res. 36 (6) (2006) 1023–1031.
[12] W. Nocun –Wczelik, Effect of Na and Al on the phase composition and morphology of autoclaved calcium silicate hydrates, Cem. Concr. Res. 29 (11) (1999) 1759–1767.
[13] M. Tsuji, S. Komarneni, Alkali Metal ion excange selectivity of Al-substituted tobermorite, J. Mater. Res. 4 (3) (1989) 698–703.
[14] S.A. El-Korashy, Cation exchange of alkali metal hydroxides with some hydrothermally synthesized calcium silicate compounds, J. Ion Exchange. 15 (1) (2004) 2–9.
[15] S. Komarneni, E. Breval, D.M. Roy, Reactions of some calcium silicate with metal cations, Cem. Concr. Res. 18 (1988) 204–220.
[16] K. Inoue, S. Tsunematsu, H. Yamada, Characteristic of removal of heavy metals by Al-substituted tobermorites, Gypsum Lime 229 (1990) 413–418.
[17] J. Reinik, I. Heinmaa, J.P. Mikkola, U. Kirso, Hydrothermal alkaline treatment of oil shale ash for synthesis of tobermorites, Fuel 86 (2007) 669–676.
[18] S.Y. Hong, F.P. Glasser, Alkali sorption by C–S–H and C–A–S–H gels — part II. Role of alumina, Cem. Concr. Res. 32 (7) (2002) 1101–1111.
[19] G.K. Sun, J. Francis Young, R. James Kirkpatrick, The role of Al in C–S–H: NMR, XRD, and compositional results for precipitated samples, Cem. Concr. Res. 36 (1) (2006) 18–29.
[20] P. Faucon, A. Delagrave, J.C. Petit, C. Richet, J.M. Marchand, H. Zanni, Aluminum incorporation in calcium silicate hydrates (C–S–H) depending on their Ca/Si ratio, J. Phys. Chem. B 103 (1999) 7796–7802.
[21] N. Meller, C. Hall, K. Kyritsis, G. Giriat, Synthesis of cement based on CaO–Al2O3–SiO2–H2O (CASH) hydroceramics at 200 and 250 C: ex-situ and in-situ diffraction, Cem. Concr. Res. 37 (2007) 823–833.
[22] N. Meller, C. Hall, J. Phipps, A new phase diagram for the CaO–Al2O3–SiO2–H2O hydroceramic system at 200 C, Mater. Res. Bull. 40 (2005) 715–723.
[23] S. Kwan, J. Thompson, M.W. Grutzeck, Structures and phase relations of aluminum-substituted calcium silicate hydrate, J. Am. Ceram. Soc. 79 (4) (1996) 967–971.
[24] M.D. Andersen, H.J. Jakobsen, J. Skibsted, Incorporation of aluminium in the calcium silicate hydrate (C–S–H) of hydrated Portland cements: a high-field ^{27}Al and ^{29}Si MAS NMR investigation, Inorg. Chem. 42 (7) (2003) 2280–2287.
[25] P. Faucon, J. Claude-Petit, Silicon substituition for aluminium in Calcium Silicate Hidrate, J. Am. Ceram. Soc. 82 (5) (1999) 1307–1312.
[26] E.I. Al-Wakeel, S.A. El-Korashy, S.A. El-Hemaly, M.A. Rizk, Divalent ion of heavy metal cations by (aluminum + alkali metals) - substituted synthetic 1.1 nm-tobermorite, J. Mater. Sci. 36 (2001) 2405–2415.
[27] M. Miyake, M. Iwaya, T. Suzuki, Aluminum-substituted gyrolite as cation exchanger, J. Am. Ceram. Soc. 73 (11) (1990) 3524–3527.
[28] 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.
[29] A. Stumm, K. Garbev, G. Beuchle, L. Black, P. Stemmermann, R. Nuesch, Incorporation of zinc into calcium silicate hydrates, Part I: Formation of C–S–H (I) with C/S = 2/3 and its isochemical counterpart gyrolite, Cem. Concr. Res. 35 (2005) 1665–1675.
[30] J. Tits, E. Wieland, C.J. Müller, C. Landesman, M.H. Bradbury, Strontium binding by calcium silicate hydrates, J. Colloid Interface Sci. 300 (1) (2006) 78–87.
[31] N.J. Coleman, Interactions of Cd(II) with waste-derived 11 Å tobermorites, Sep. Purif. Technol. 48 (1) (2006) 62–70.
[32] O.P. Shrivastava, S. Komarneni, E. Breval, Mg^{2+} uptake by synthetic tobermorite and xonotlite, Cem. Concr. Res. 21 (1991) 83–90.
[33] O.P. Shrivastava, S. Komarneni, Cesium selectivity of (Al + Na) substituted tobermorite, Cem. Concr. Res. 24 (3) (1994) 573–579.
[34] N.K. Labhesetwar, O.P. Shrivastava, Iron calcium ion exchange reaction in cement hydration phase 11 Å tobermorite, Ind. J. Chem. Sec. A 27 (11) (1988) 999–1001.
[35] O.P. Shrivastava, P.K. Wattal, T. Verma, Intrinsic sorption potential of Al-substituted calcium silicate hydroxy hydrate for cesium^{137}, Adv. Cem. Based Matrices 2 (2) (1995) 80–83.
[36] N.J. Coleman, Synthesis, structure and ion exchange properties of 11 angstrom tobermorites from newsprint recycling residue, Mater. Res. Bull. 40 (11) (2005) 2000–2013.
[37] S.H. Kosmatka, B. Kerkhoff, W.C. Panarese, Design and Control of Concrete Mixtures, 14th EditionPortland Cement Association, Skokie, Illinois, 2002.
[38] Z. Shauman, Influence of SO_4^{2-} ions on the formation of 11 Å tobermorite, The 2nd international Symposium on Science and Research in Silicate Chemistry, Brno, 1972, pp. 25–39.
[39] S.A. Krzheminskij, Hydrothermal treatment of silicate materials, Stroyizdat, Moscow, Russia, 1974 in Russian.
[40] S.A. Krzheminskij, L.A. Krojchuk, Z.P. Kotikova, L.M. Brusnitskaja, The influence of gypsum on the reaction rate of calcium oxide during hydrothermal treatment of silicate products and its strength, Collect. VNIISTROM Works 24 (52) (1972) 15–22 in Russian.
[41] P.P. Budnikov, L.A. Krojchuk, Hydrothermally treated building materials, J.D.M. Mendeleev Chem. Soc. 13 (2) (1986) 176–181 in Russian.
[42] I.A. Veretinskaja, Influence of sulfur compounds on formation of calcium silicate hydrates in aerated concrete, Proceedings: Calcium silicate hydrates and their application, Kaunas, 1980, pp. 41–42, in Russian.
[43] M. Sakiyama, T. Mitsuda, Influence of gypsum on formation of tobermorite, Review of 31st General Meeting, The Cement Association of Japan, Tokyo, 1977, pp. 35–36.
[44] K.K. Kuatbaev, Physical and chemical properties of hardening and durability processes of hydrothermally treated aliuminum silicate and silicate materials, PhD thesis, Almaty (1982). (in Russian).
[45] S.I. Grabko, Research of an opportunity of optimization of technology shale-sand hydrothermally treated concrete, PhD thesis, Tallinn (1975). (in Russian).
[46] R. Vektaris, B. Leskauskas, K. Sasnauskas, The influence of gypsum additives on formation process of low-base calcium silicate hydrates, Proceedings: Research of building materials, Vilnius, 1987, pp. 74–85, in Russian.
[47] R.Vektaris. Compounds formation in the CaO–SiO_2–$CaSO_4$–H_2O system and application of products of hydrothermal synthesis, PhD thesis, KPI, Kaunas (1988). (in Russian).
[48] B.H. Vinogradov, L.A. Krojchuk, Formation and stability of calcium silicate hydrate CSH(A), Russ. J. Appl. Chem. 48 (1) (1975) 28–32 in Russian.
[49] P.P. Budnikov, L.A. Krojchuk, B.H. Vinogradov, Crystallization of calcium silicate hydrates at presence of gypsum and aliuminum oxide, Dokl. Akad. Nauk SSSR 173 (3) (1967) 630–633 in Russian.
[50] R. Jauberthie, M. Temimi, M. Laquerbe, Hydrothermal transformation of tobermorite gel to 10 Å tobermorite, Cem. Concr. Res. 26 (9) (1996) 1335–1339.
[51] L. Števula, M. Harman, I. Horvath, K. Putyera, The mineral gyrolite and its stability under hydrothermal conditions, Ceram.-Silik. 34 (1990) 315–330.
[52] Y. Okada, T. Masuda, H. Ishida, Behavior of silicate anions on the formation processes of gyrolite followed by ^{29}Si NMR, J. Ceram. Soc. Jpn. 103 (2) (1995) 124–127.
[53] R. Siauciunas, K. Baltakys, Formation of gyrolite during hydrothermal synthesis in the mixtures of CaO and amorphous SiO_2 or quartz, Cem. Concr. Res. 34 (2004) 2029–2036.
[54] 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 Ca16Si24O60(OH)8 14H2O, Am. Mineral. 87 (2002) 533–541.
[55] 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.