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Formation and stability of C–S–H (I) of various degrees of crystallinity in the $Ca(OH)_2$/CaO–Hi-Sil–H_2O system

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The stability and crystal morphology of C–S–H (I) in the CaO/$Ca(OH)_2$–Hi-Sil–H_2O systems and a sequence of formation of the intermediary compound has been examined. Two series of samples, with different ratios of CaO to SiO_2 were used in the experimental tests. The molar ratio CaO/SiO_2 of primary mixtures was 1.0. Hydrothermal synthesis was carried out under the saturated steam pressure at temperatures of 90, 110, 130, 150 and 175 °C; the duration of isothermal curing was 2–72 h. It was determined that an increase of temperature significantly influences the stability, morphology and degree of crystallinity of C–S–H (I). It was found that C–S–H (I) is stable in the ranhe 90–130 °C. The overall morphology of C–S–H varies from the common fibrous type to irregular grains forming a reticular network. The compositions of intermediate products and of final products can be changed by adding calcium containing components ($Ca(OH)_2$, CaO). In the mixtures with $Ca(OH)_2$, an intermediate compound is C–S–H (I) and the final product is xonotlite. Meanwhile, in the mixtures with CaO, the main intermediate compounds are Z phase and C–S–H (I), and the main product is gyrolite.

Key words: *calcium silicate hydrates; C–S–H (I); xonotlite; gyrolite; X-ray diffraction*

1. Introduction

Calcium silicate hydrates (C–S–H) are an important group of silicate minerals with compositions varying over a large range of CaO/SiO_2 ratios (0.44–3.0) and crystallographic structures from amorphous to well-crystalline [1–8]. Calcium silicate hydrates are the prime candidates for heavy metal binding because of their abundance and appropriate structure [9–13]. Besides, these compounds are of great importance in cement chemistry, where C–S–H gels are the main reaction products and primary binding phases in Portland cement.

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The conditions of formation and stability of various calcium silicate hydrates are governed by various parameters influencing the kinetics of the reaction and even the microstructure of the products, such as temperature, stirring, the presence of foreign ions and their concentrations [14–22].

The C–S–H (I) phase is a nearly amorphous gel with the specific surface exceeding 150 m^2/g. It is composed of a few elementary layers forming wrinkled foils whose thickness amounts to several nanometers. The substitution of aluminum in the octahedral or tetrahedral sheets of the C–S–H readily modifies the charge of the crystal lattice and might have a direct influence on the material macroscopic properties (cohesion, retention or release of pollutants, durability, etc.) [23, 24]. Hydrothermal treatment of lime–silica mixtures under saturated steam pressures below 250 °C usually gives ill-crystallized calcium silicate hydrates as an initial product, which reacts further to give crystalline calcium silicate hydrates. Mitsuda et al. [25] found that C–S–H (I) was always formed as an initial product of the crystalline phase. The authors presented the following reaction sequence in the temperature range 120–210 °C when the CaO/SiO_2 molar ratio was equal to 1:

C–S–H (crumpled foils) → C–S–H (mixture of crumpled foils and fibre aggregates) → xonotlite

These results for crystalline phases formed after C–S–H agreed with those reported by many authors [26–28].

It is well known that C–S–H (I) phase is thermodynamically unstable and shows a tendency to crystallize [29, 30]. It transforms to tobermorite but this processes is very slow, probably due to difficulties in nucleation. Elevated temperatures accelerate the transformation, high pressure seems to be even more efficient. In the majority of cases, the product of the transformation yields a mixture of C–S–H (I) and tobermorite [31]. Besides, C–S–H products exhibit similarities to the clay minerals in the crystal structure assembly. They comprise composite sheets made up of distorted calcium hydroxide sheets flanked on both sides by parallel rows of wollastonite type chains. The remaining calcium atoms are positioned in interlayer regions. A pH dependent surface charge is the result of silanol sites associated with the bridging silica tetrahedra or end chain tetrahedra [3, 32, 33].

According to the collected reference data, there are only a few published results (and even these are not comprehensive) about stability and crystal morphology of C–S–H (I) having different degrees of crystallinity. Besides, every year many companies cause a lot of environmental pollution in all countries of the world and this has become a really serious problem. Thus, these by-products are expedient to use as secondary raw materials. In particular, the compounds which have silicon and calcium components can be applied for the synthesis of calcium silicate hydrates.

The aim of this paper was to examine the stability and crystal morphology of C–S–H (I) in the $CaO/Ca(OH)_2$ and Hi-Sil mixtures as well as to analyze and explain the formation sequence of intermediary compounds.

2. Experimental

The following materials were used in this work: calcium hydroxide $Ca(OH)_2$ (of 98 % purity, a product of ACROS ORGANICS, Belgium), industrial CaO (loss of ignition 23%, Manufacturer Pigeon Chaux, Saint Pierre La Cour, France) and silica fume (Hi-Sil 255C-D obtained from PPG, amorphous silica > 87 %, crystalline silica < 0.01 %, Na_2SO_4 < 2 %, pH = 6.3, surface area – 180 m^2/g).

Two series of samples, with different ratios of CaO to SiO_2, were used in the experimental tests. The molar ratio CaO/SiO_2 of primary mixtures was 1.0. Hydrothermal synthesis was carried out under the saturated steam pressure at 90, 110, 130, 150 and 175 °C; the duration of isothermal curing was 2, 8, 24 or 72 hours. After synthesis, samples were removed from the teflon cells and transferred to an air conditioned chamber with relative humidity of 55% at 20 °C and sieved through a sieve with a 50 μm mesh.

The XRD data were collected with Philips PW 3710 X-ray diffractometer with the Bragg–Brentano geometry using Ni-filtered CuK_α radiation, 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 $2\theta = 0.02°$.

SEM (JEOL-JSM-6301F) of the samples was performed using an accelerating voltage of 9 kV and a working distance of 15 mm.

FTIR spectra were obtained with a Perkin Elmer spectrometer FTIR system spectrum X. 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 a spectral resolution of 1 cm^{-1}.

3. Results and discussions

In the $Ca(OH)_2$–Hi-Sil–H_2O system, after 4 h at 90 °C C–S–H (I) (*d* spacing – 0.573, 0.304, 0.281, 0.210, 0.183 nm) and $CaCO_3$ (*d* spacing – 0.385, 0.304, 0.250, 0.229, 0.210, 0.191, 0.188 nm) formed (Fig. 1, curve 1).

The results of scanning electron microscopy were confirmed by the XRD data: amorphous, with no definite crystal structure aggregations typical of a low crystalline degree C–S–H (I) were identified in the products (Fig. 2a).

Upon extending the duration of synthesis to 8, 24 or 72 h, the same compounds (C–S–H (I) and $CaCO_3$) were obtained (Fig. 1). SEM analysis indicated that even after 72 h of isothermal curing at 90 °C, the crystal structure of the products remained practically unchanged (Fig. 2 b).

In order to determine the influence of temperature on the stability and crystal morphology of C–S–H (I), the synthesis was carried out at higher temperatures.

X-ray diffraction curves of the synthesized compounds show that similar amounts of C–S–H (I) (*d* spacing – 0.534, 0.304, 0.281, 0.210, 0.183 nm) and calcite (*d* spacing – 0.386, 0.304, 0.250, 0.229, 0.210, 0.192, 0.188 nm) were formed irrespective of the

temperature of synthesis (110, 130 °C) and its duration (4, 8, 24, 72 h), because the intensities of the main diffraction peaks are similar (Fig. 3, curve 1).

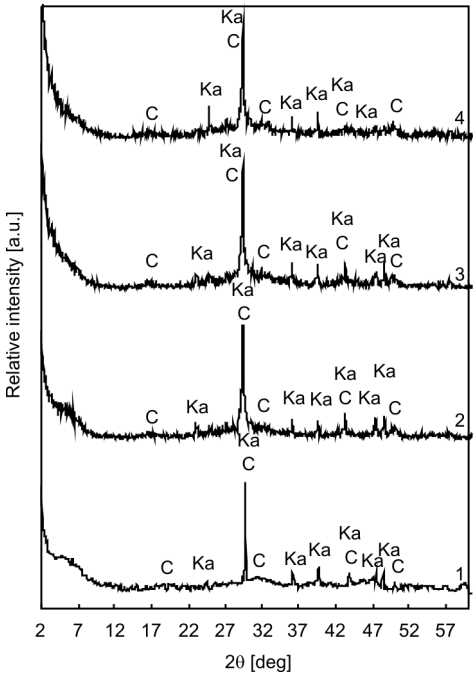

Fig. 1. X-ray diffraction patterns of products of the synthesis; the duration of the hydrothermal synthesis at 90 °C, h: 1 – 2, 2 – 8, 3 – 24, 4 – 72; C – C–S–H (I), Ka – calcite

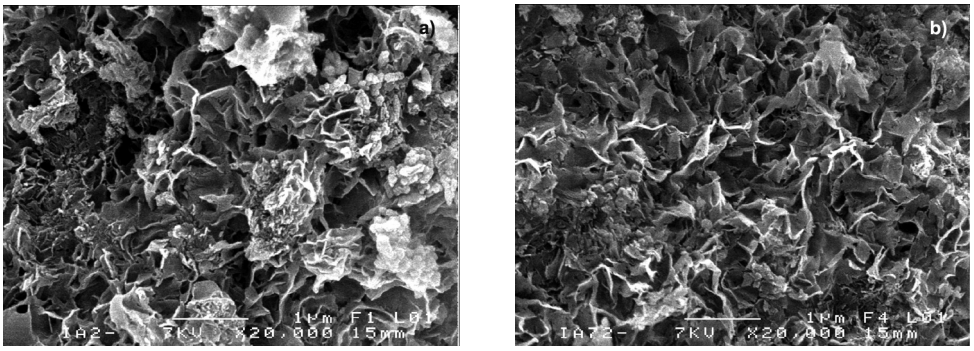

Fig. 2. SEM micrographs of the products of the synthesis; the duration of hydrotermal treatment at 90 °C was: a) 2 h, b) 72 h

The same reaction sequence was proved by SEM analysis. SEM data shows that the overall morphology of C–S–H can actually vary from the common fibrous type to irregular grains forming a reticular network (Fig. 4).

At the beginning of the reaction at 150 °C the same products dominated as at lower temperature (Fig. 5). The FTIR spectra showed typical bands of C–S–H (I): the band at ~970 cm^{-1} due to the Si–O stretching mode of nonbinding oxygens and the

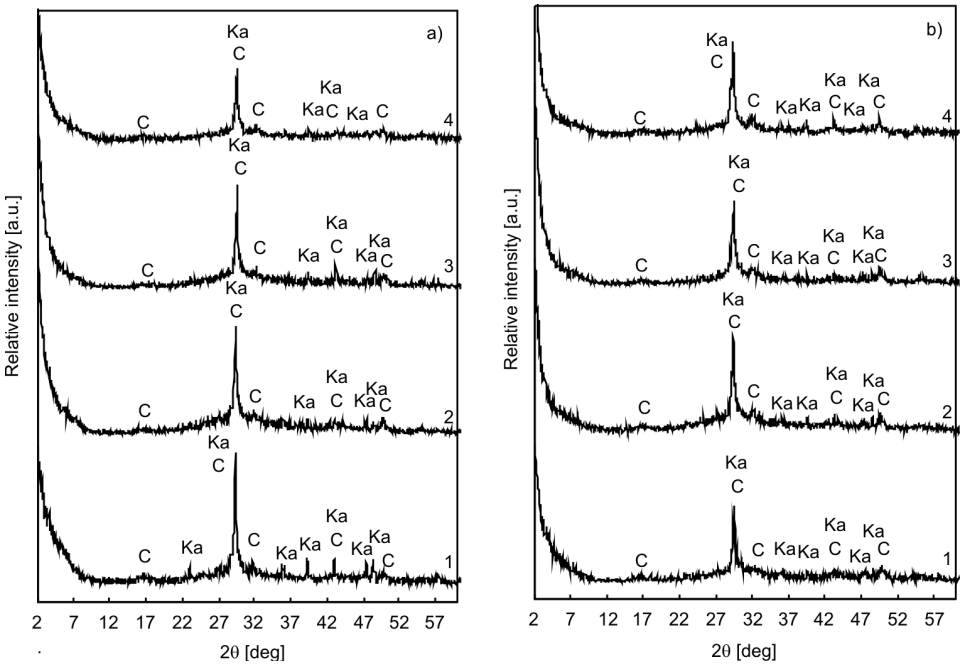

Fig. 3. X-ray diffraction patterns of the products of the synthesis; the duration of hydrothermal synthesis at 110 °C (a) and 130 °C (b), h: 1 – 4, 2 – 8, 3 – 24, 4 – 72; C – C–S–H (I), Ka – calcite

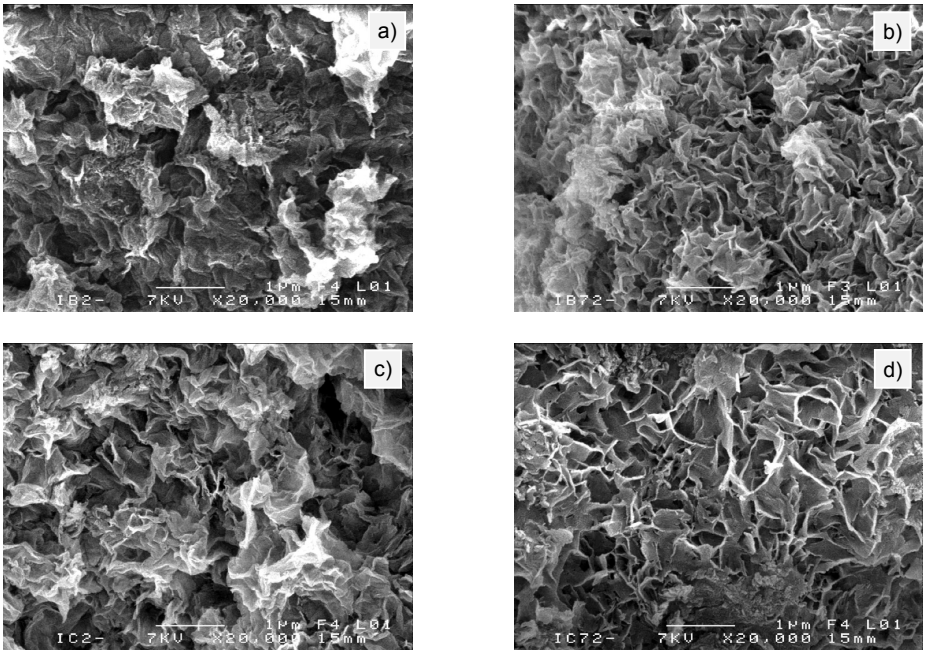

Fig. 4. SEM micrographs of the products of the synthesis. Duration of hydrotermal curing at 110 °C (a, b) and 130 °C (c, d): a) and c) – 2 h, b) and d) 72 h

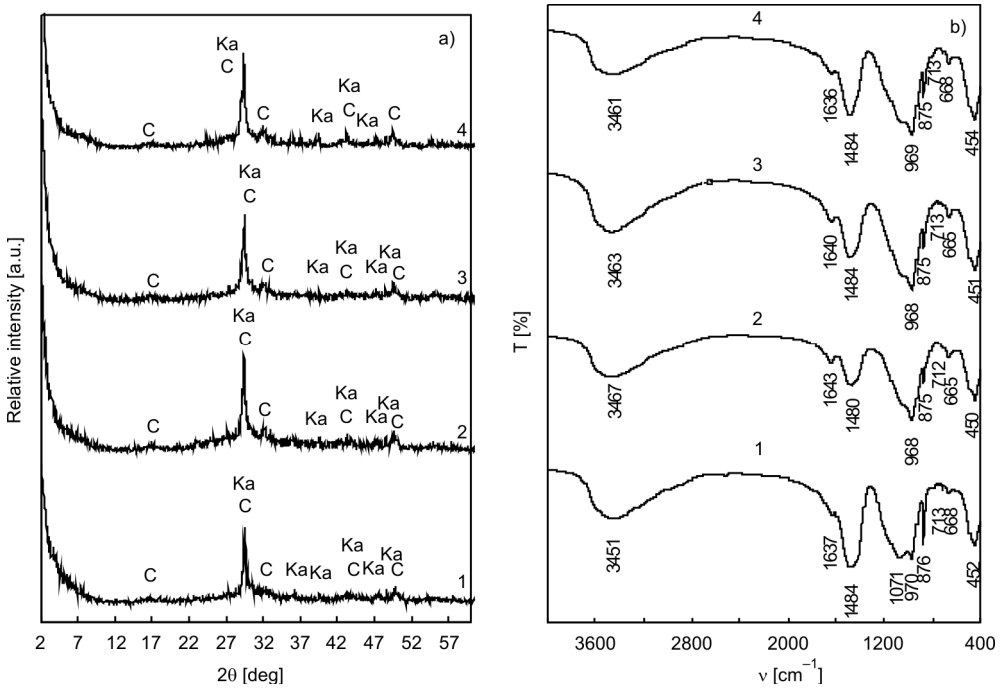

Fig. 5. XRD patterns (a) and FTIR spectra (b) of the products of the synthesis; the duration of the hydrothermal synthesis at 150 °C: 1 – 2 h, 2 – 8 h, 3 – 24 h, 4 – 72 h; C – C–S–H (I), Ka – calcite

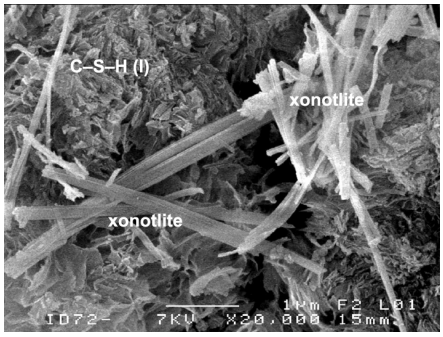

Fig. 6. SEM micrographs of the products of the synthesis; duration of hydrotermal curing at 150 °C was 72 h

band at ~668 cm^{-1} due to the Si–O–Si bonds. The broad band at ~3451 cm^{-1} was due to the stretching vibration of –OH groups in H_2O hydroxyls with a wide range of hydrogen bonding strength. Further water peak at about 1637 cm^{-1} confirmed $\delta(H_2O)$ stretching vibration. Moreover $\nu(CO_3^{2-})$ vibrations at 713, 876, 1484 cm^{-1} were found in the IR spectra (Fig. 5b).

It should be underlined that after 72 hours of isothermal curing unexpected results were obtained. The accumulation of two morphologous crystals can be seen in SEM micrographs: C–S–H (I) characteristic irregular shape crystals and long, needle/plate shape xonotlite crystals that are formed as on C–S–H (I) grains and in the interlayers between them (Fig. 6).

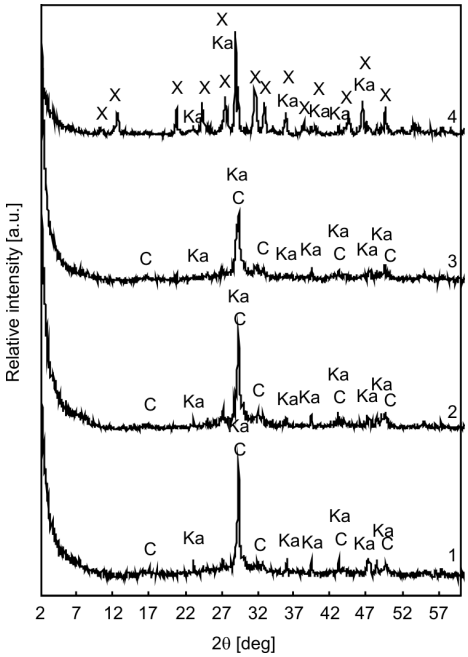

Fig. 7. X-ray diffraction patterns of the products of the synthesis; the duration of hydrothermal synthesis at 175 °C: 1 – 2 h, 2 – 8 h, 3 – 24 h, 4 – 72 h; C – C–S–H (I), X – xonotlite, Ka – calcite

The formation of xonotlite is confirmed by XRD studies only after 72 h at 175 °C: the main peak with *d* spacing – 0.703 nm, which is specific to xonotlite, was identified (Fig. 7, curve 4, *d* spacing – 0.703; 0.426; 0.364; 0.271; 0.250; 0.228 nm). This agrees with SEM data (Fig. 8).

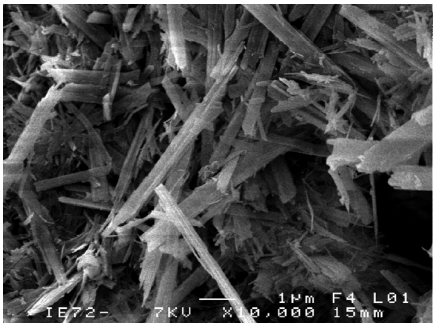

Fig. 8. SEM micrographs of the products of the synthesis; the duration of hydrotermal curing at 175 °C was 72 h

According to the obtained results, the reactions of new compound formations, in the mixture of CaO and Hi-Sil at 90–175 °C, occur in the following sequence:

$$\mathrm{Ca(OH)_2} + \text{Hi-Sil} + \mathrm{H_2O} \begin{matrix} \nearrow \mathrm{CaCO_3} \\ \searrow \mathrm{C-S-H\ gel} \end{matrix} \rightarrow \mathrm{C-S-H\ (I)} \rightarrow \text{xonotlite},\ \mathrm{CaCO_3}$$

It should be stressed that the mechanism of hydrothermal reactions and the sequence of the compounds formed in the CaO–Hi-Sil–H_2O mixture are quite different,

as another component containing Ca^{2+} was used. The data of XRD analysis showed that at 90 °C and 110 °C only one the products of the – C–S–H (I) (*d* spacing – 0.567, 0.304, 0.280, 0.209, 0.182 nm) and $CaCO_3$ (*d* spacing – 0.304, 0.249, 0.228, 0.209, 0.192, 0.188 nm) were formed (Fig. 9).

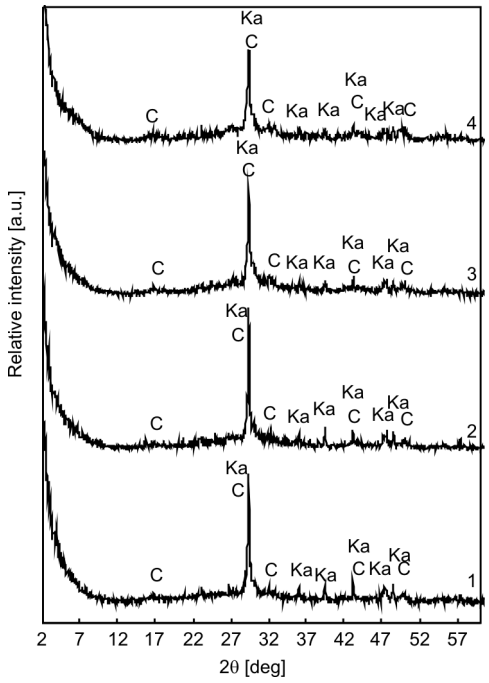

Fig. 9. X-ray diffraction patterns of the products of the synthesis; the duration of hydrothermal synthesis at 110 °C: 1 – 2 h, 2 – 8 h, 3 – 24 h, 4 – 72 h; C – C–S–H (I), Ka – calcite

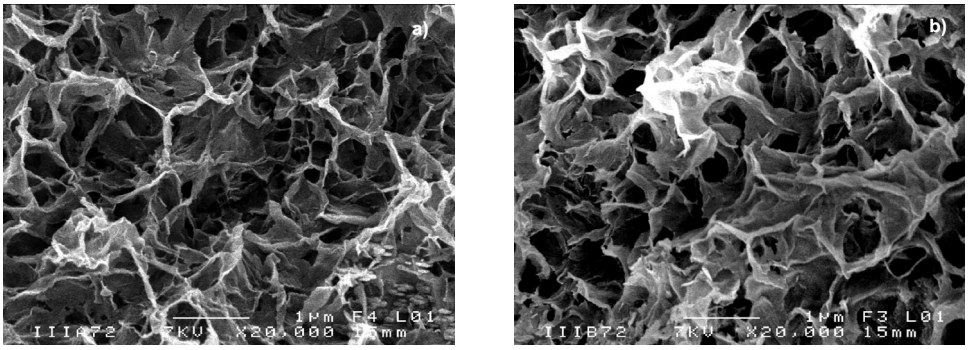

Fig. 10. SEM micrographs of the products of the synthesis; duration of hydrotermal curing at 90 °C (a) and 110 °C (b) was 72 h

Moreover, aggregations of the same crystal structure as in the $Ca(OH)_2$–Hi-Sil –H_2O mixture were identified after 72 h of isothermal curing at 90 and 110 °C (Fig. 10). It should be underlined that at 130 °C the degree of crystallinity of C–S–H (I) is higher than at 90 °C or 110 °C (Figs. 11, 12).

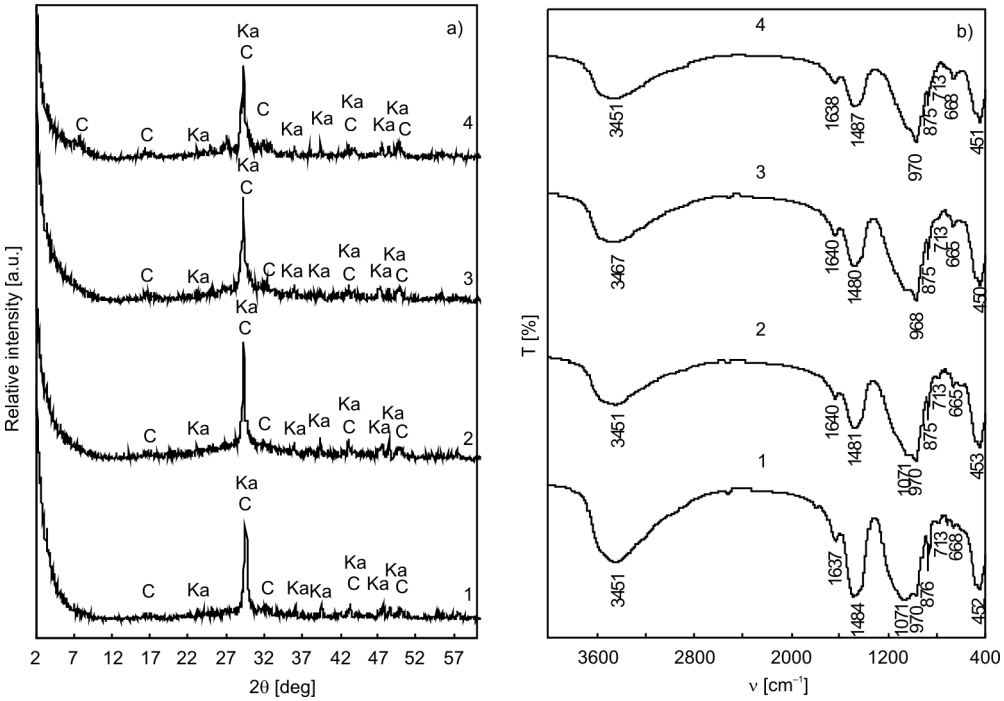

Fig. 11. X-ray diffraction patterns (a) and FT-IR spectra (b) of the products of the synthesis; the duration of the synthesis at 130 °C: 1 – 2 h, 2 – 8 h, 3 – 24 h, 4 – 72 h; C – C–S–H (I), Ka – calcite

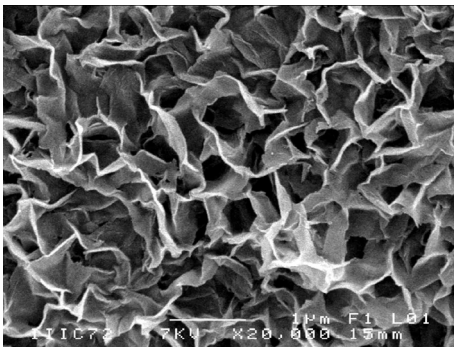

Fig. 12. SEM micrographs of the products of the synthesis; the duration of hydrotermal curing at 130 °C was 72 h

X-ray diffraction patterns show basic reflections characteristic of a semi-crystalline C–S–H (I) type calcium silicate hydrate already with larger *d* spacing – 1.2440; 0.304; 0.278; 0.183 nm (Fig. 11a, curve 4).

The data of SEM analysis showed that the overall morphology of C–S–H (I) varies from the common fibrous type to irregular plates (Fig. 12). Moreover, FTIR spectra of semi-crystalline compounds contain a characteristic set of bands at 3451, 1638, 1487, 970, 875, 668, 451 cm^{-1} (Fig. 11).

After 72 h of isothermal curing at 150 °C, unexpected results were also obtained: C–S–H (I) starts regrouping into low-base calcium silicate hydrate gyrolite gel

(*d* spacing – 2.230, 0.420, 0.304, 0.280, 0.210, 0.183 nm) and Z phase (*d* spacing – 1.522, 0.304, 0.280, 0.183 nm) (Fig. 13, curve 4). These results were confirmed by SEM analysis: gyrolite gel and Z phase tend to crystallize in clusters of plates, while C–S–H (I) forms fibrous material (Fig. 14).

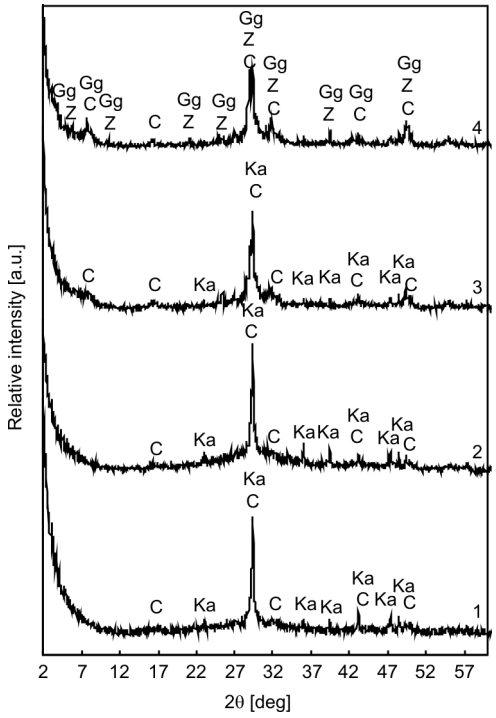

Fig. 13. X-ray diffraction patterns of the products of the synthesis; the duration of hydrothermal synthesis at 150 °C was: 1 – 2 h, 2 – 8 h, 3 – 24 h, 4 – 72 h; C – C–S–H (I), Ka – calcite, Gg – gyrolite gel, Z – Z phase

Fig. 14. SEM micrographs of the products of the synthesis; duration of hydrotermal curing at 150 °C was 72 h

As far as we know, this is the first evidence that C–S–H (I) is unstable in those mixtures for which the molar ratio (CaO/SiO_2) of the primary mixture is equal to 1.0. Besides, in CaO–Hi-Sil–H_2O mixtures this compound recrystallizes into calcium silicate hydrates when in $Ca(OH)_2$–Hi-Sil–H_2O system under the same conditions (72 h at 150 °C), xonotlite and calcite dominate in the products.

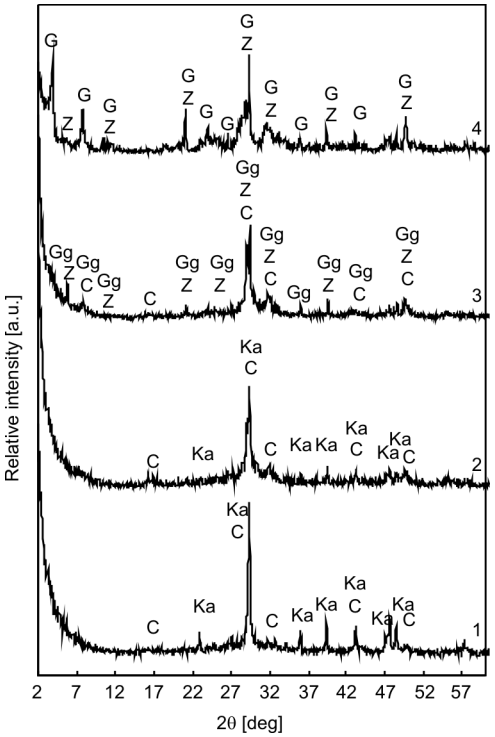

Fig. 15. X-ray diffraction patterns of the products of the synthesis; the duration of hydrothermal synthesis at 175 °C: 1 – 2 h, 2 – 8 h, 3 – 24 h, 4 – 72 h; C – C–S–H (I), Ka – calcite, Z – Z phase, Gg – gyrolite gel, G – gyrolite

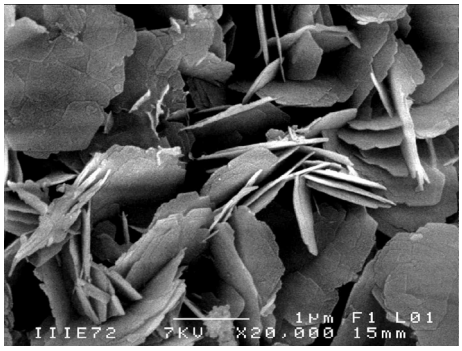

Fig. 16. SEM micrograph of the products of the synthesis; the duration of hydrotermal curing at 175 °C was 72 h

The data obtained at 175 °C proved that C–S–H (I) is a metastable compound, because after 24 h of synthesis, low base calcium silicate hydrates Z phase (*d* spacing – 1.501, 0.418, 0.303, 0.281, 0.184 nm) and gyrolite gel (*d* spacing – 2.232, 0.360, 0.303, 0.281, 0.248, 0.228, 0.209, 0.190, 0.184 nm) were prevalent (Fig. 15, curve 3). Furthermore, within 72 h of hydrothermal treatment, almost all the Z phase finishes transferring into gyrolite (Fig. 15, curve 4). These results were confirmed by SEM data: gyrolite crystallized into well-crystalline plates (Fig. 16).

Thus, in the CaO–Hi-Sil–H_2O system in the temperature range from 90 °C to 175 °C, xonotlite did not form even after 72 h of hydrothermal curing. The sequence of compounds to be formed during the synthesis is as follows:

$$\mathrm{CaO + Hi\text{-}Sil + H_2O} \nearrow \begin{matrix} \mathrm{CaCO_3} \\ \mathrm{C-S-H\ gel} \end{matrix} \searrow \rightarrow \mathrm{C-S-H(I),\ CaCO_3}$$

$$\rightarrow \begin{cases} \text{gyrolite gel} \\ \text{Z phase} \\ \mathrm{C-S-H\ (I)} \end{cases} \rightarrow \begin{cases} \text{gyrolite} \\ \text{Z phase} \end{cases}$$

The obtained results showed that the by-products can be used as secondary raw materials in the synthesis of calcium silicate hydrates. Meanwhile, the formation conditions and stability of aforementioned compounds depend on calcium containing component ($Ca(OH)_2$, CaO), which change the composition of intermediate and final products of the synthesis.

4. Conclusion

Increase in temperature significantly influences the stability, morphology and degree of crystalline of C–S–H (I) in the temperature range from 90 °C to 175 °C. It was found that in the $CaO/Ca(OH)_2$ and Hi-Sil mixtures when the molar ratio of the primary mixture CaO/SiO_2 equals 1.0, C–S–H (I) is stable in the temperature between 90 and 130 °C. The overall morphology of C–S–H varies from the common fibrous type to irregular grains forming a reticular network.

Calcium containing components ($Ca(OH)_2$, CaO) change the composition of intermediate and final products of the synthesis. In the mixtures with $Ca(OH)_2$, an intermediate compound is C–S–H (I) and the final product is xonotlite. Meanwhile, in the mixtures with CaO, the main intermediate compounds are Z phase and C–S–H (I), and the main product is gyrolite. In both mixtures, calcite prevails at the beginning of the synthesis and remains in the products in almost all conditions under investigation.

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