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Influence of CaO reactivity on the formation of low-base calcium silicate hydrates

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The influence of CaO reactivity on the formation of calcium silicate hydrates in the $CaO–SiO_2·nH_2O–H_2O$ system has been determined when the CaO/SiO_2 molar ratio was equal to 0.83 and 1.0. In a pure $CaO–SiO_2·nH_2O–H_2O$ system, with CaO/SiO_2 = 0.83, C–S–H (I) is rather stable, and at 175 °C, even after 72 h, only partially recrystallizes into 1.13 nm tobermorite. Meanwhile, in the mixtures with less reactive CaO (96%), the stoichiometric composition (CaO/SiO_2) of products of the synthesis varies from 0.66 to 0.83. When the CaO/SiO_2 molar ratio in the initial mixture is equal to 1.0, the CaO reactivity has a significant effect on the composition of products forming in hydrothermal conditions. The products of the syntheses were characterized by X–ray diffraction analysis, simultaneous thermal analysis and Fourier transform infrared spectroscopy.

Keywords: *calcium silicate hydrate; 1.13 nm tobermorite; gyrolite; CaO reactivity*

1. Introduction

The most common calcium silicate hydrates found in nature, produced in laboratories and formed in silicate products during hydrothermal treatment – or in autoclaved or hot-pressed materials – are C–S–H (I), 1.13 nm tobermorite, xonotlite, gyrolite. The formation of these calcium silicate hydrates depends on the duration and temperature of hydrothermal synthesis, stoichiometric composition of the initial mixture (CaO/SiO_2 (C/S) molar ratios), granulometric composition (grading) and strain of the raw materials, the additives used, mixing intensity and other factors [1–5].

Low-base (C/S = 0.6–1.5) and high-base (C/S = 1.5–2.0) calcium silicate hydrates belong to the set of key binding compounds [6]. They can be used as fillers for the production of rubber, plastics, paper, paint; for cleaning water contaminated with heavy and radioactive metal ions, for non-asbestos heat insulations, for adsorbents of

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organic and inorganic effluents, cation exchangers [7]. Therefore, calcium silicate hydrates formed under hydrothermal conditions are the subject of numerous scientific studies.

The 1.13 nm tobermorite is the most prevalent among calcium silicate hydrates found in nature and obtained during autoclave treatment. This compound was first described by Heddle [8]. Tobermorite is known to have four different strains: 0.9 nm tobermorite – riversidite, 1.13 nm tobermorite, 1.4 nm tobermorite – plombierite, and clinotobermorite [9–11]. The 1.13 nm tobermorite $Ca_5(Si_6O_{18}H_2)\cdot 4H_2O$ can be reproduced in the laboratory in hydrothermal conditions when C/S = 0.8–1.0 [2]. The typical interplatelet distances *d* of 1.13 nm tobermorite are 1.13 and 0.297 nm.

From the wollastonite group of calcium silicate hydrates, xonotlites $Ca_6(Si_6O_{17})(OH)_2$ are of great practical importance and interest [3, 4]. This compound can be synthesized at 190–400 °C when the molar ratio of the mixture is C/S = 1.0. Xonotlite is characterized by an interplatelet distance *d* of 0.7 nm [12]. Nocuń–Wczelik reports that synthesis of xonotlite highly depends on the SiO_2 strain and the temperature and duration of synthesis [13] and that xonotlite may be formed directly, without the formation of an intermediate mineral – 1.13 nm tobermorite.

Gyrolite ($2CaO\cdot 3SiO_2\cdot 2.5H_2O$), calcium silicate hydrate, rarely occurs as a natural mineral together with with zeolites as low-temperature hydrothermal replacement product of basic igneous rock. Synthetic gyrolite was hydrothermally synthesized by Flint et al. [14]. They indicated that after 6–42 days of hydrothermal synthesis at 150–350 °C, the only product – gyrolite forms when the C/S ratio changes from 0.5 to 0.66. Mackay and Taylor [15] synthesized this compound by isothermal curing at 150 °C within 76 days of. Later on, other scientists continued studies on the synthesis of gyrolite [16–18]. It was declared that gyrolite is stable at 120–200 °C in hydrothermal conditions under a saturated steam pressure. Truscottite ($Ca_{14}Si_{24}O_{58}(OH)_8\cdot 2H_2O$) forms at the temperature higher than 200 °C, although metastable gyrolite may be obtained at temperatures up to 270 °C. It is assumed that gyrolite forms only at a temperatures higher than 120 °C. The parameters of hydrothermal synthesis of gyrolite in unstirred suspensions, when initial mixtures were composed from CaO and $SiO_2\cdot nH_2O$ or quartz, were determined elsewhere [19]. The results of the research showed that the optimal temperature of the synthesis of gyrolite is rather high (approximately 200 °C) and that the duration is long (ca. 32 h) when amorphous $SiO_2\cdot nH_2O$ is used as the SiO_2 component.

Much scientific research is focused on the influence of calcium strains SiO_2 on the formation of calcium silicate hydrate [2, 5, 20]. Not much data has been published on the effects of reactivity of another raw material, CaO, on the synthesis of calcium silicate hydrates.

The aim of this work was to analyse the influence of reactivity of CaO on the formation of 1.13 nm tobermorite and xonotlite, as well as to analyse and explain the sequence of formations of intermediary compounds.

2. Experimental

The following reagents were used as starting materials: fine-grained $SiO_2 \cdot nH_2O$ (Reachim, Russia, ignition losses 21.28%, specific surface area S_a = 1155 m²/kg by Blaine), CaO (free CaO = 99.96%, S_a = 548 m^2/kg, time of lime slaking τ = 135 s, temperature of lime slaking 96 °C, Reachim, Russia) and CaO (free CaO = 96%, S_a = 320 m^2/kg, time of lime slaking τ = 430 s, temperature of lime slaking 94 °C, Reachim, Russia) were additionally burned at 1000 °C for 0.5 h.

The syntheses of calcium silicate hydrates were carried out in unstirred suspensions in stainless steel vessels. Calcium silicate hydrates were synthesized within 8, 16, 24 and 72 h at 175 °C using stoichiometric compositions (CaO/SiO_2 molar ratios were equal to 0.83 and 1.0, the water/solid ratio of the suspension was equal to 10.0) of the initial CaO and $SiO_2 \cdot nH_2O$ mixture. The products of the syntheses were filtered, rinsed with ethyl alcohol to prevent carbonization of materials, dried at 50 ± 5 °C and filtered through a sieve with a mesh width of 50 μm.

The X-ray powder diffraction data was collected with a DRON–6 X-ray diffractometer with the Bragg–Brentano geometry using Ni-filtered CuK_α radiation and a graphite monochromator, operating at the voltage of 30 kV and delivering an 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 carried out on a Netzsch instrument STA 409 PC applying the heating rate of 15 °C/min. The temperature ranged from 30 °C up to 1000 °C under an air atmosphere. Ceramic sample handlers and crucibles of Pt–Rh were used.

FTIR spectra were obtained with the aid of a Perkin Elmer FTIR Spectrum X system. 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}.

3. Results and discussion

After 8 h of isothermal curing at 175 °C in the Ca O–$SiO_2 \cdot nH_2O$–H_2O system, traces of 1.13 nm tobermorite (Fig. 1, curve 1, *d* spacing 1.1472, 0.5449, 0.3063, 0.2967, 0.2804, 0.1834, 0.1670 nm, the area of the endothermic effect at 220 °C is equal to 5.72 μV·s/mg, according to the tangent method) together with C–S–H (I) were formed (Fig. 1, curve 1, *d* spacing 0.3048, 0.1834 nm, the area of the exothermic effect at 833 °C is equal to 41.24 μV·s/mg according to the tangent method). By prolonging the duration of synthesis, an increasing amount of 1.13 nm tobermorite is formed in the product, due to an increase in the intensity of its characteristic diffraction peak, whose interplanar distance is *d* ~1.13 nm, and the area of the endothermic effect at 219 °C is 8.31 μV·s/mg (Fig. 1, curve 2). It should be underlined that even

after an isothermal exposure for 72 h, the identified endothermic effect (i.e., the area measuring 9.34 μV·s/mg) at 848 °C indicates that a small amount of C–S–H (I), which had insufficient time for recrystallisation into 1.13 nm tobermorite, remains in the products (Fig. 1b, curve 3). These data was confirmed by differential scanning calorimetry: at 225 °C the area of the endothermic effect increased to 18.97 μV·s/mg (Fig. 1b, curve 3).

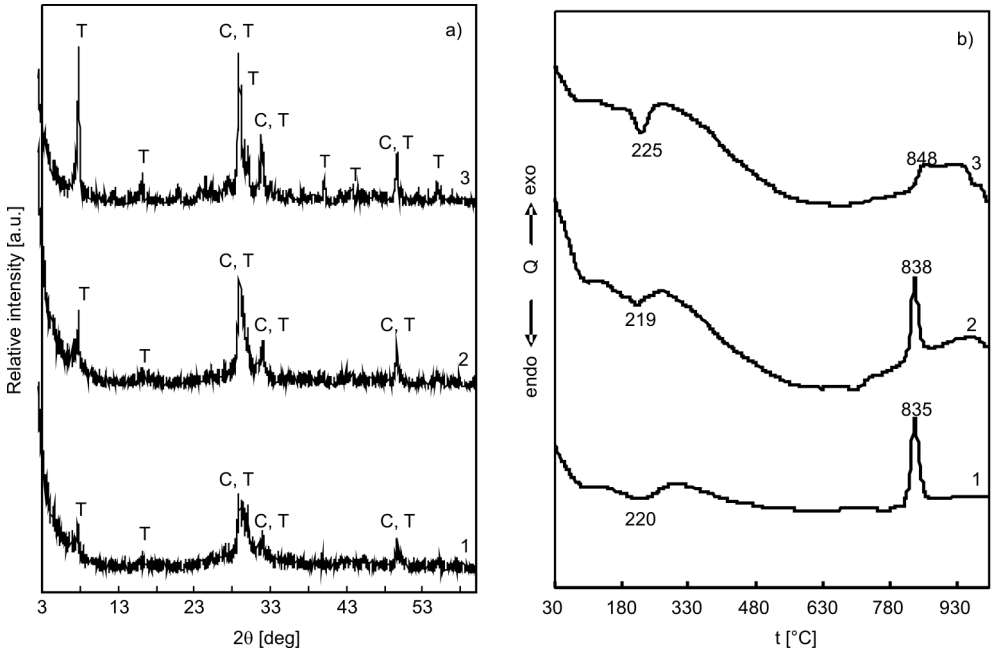

Fig. 1. X-ray diffraction patterns (a) and DSC curves (b) of the products of synthesis; the initial C/S molar ratio is equal to 0.83. Duration [h] of hydrothermal syntheses at 175 °C: 1 – 8; 2 – 16; 3 – 72; C – C–S–H (I), T – 1.13 nm tobermorite

Thus, in a pure CaO–SiO_2·nH_2O–H_2O system, C–S–H (I) which formed at the beginning of the synthesis, is sufficiently stable and at 175 °C, even after 72 h, it only partially recrystallizes into 1.13 nm tobermorite.

In mixtures with less reactive CaO (96%), changes occur not only in the sequence of the formed compounds, but also in their stability limits. After 8 h of hydrothermal synthesis, a semicrystalline calcium silicate hydrate C–S–H (I) and traces of 1.13 nm tobermorite were formed (Fig. 2, curve 1). It should be noted that 1.13 nm tobermorite becomes a dominant compound after 24 h of hydrothermal treatment (Fig. 2, curve 2). After extending the duration of isothermal curing to 72 h, unexpected results were obtained: the intensity of peaks characteristic of the 1.13 nm tobermorite in X-ray patterns decreased (Fig. 2, curve 3). Together with this compound, a low-base calcium silicate hydrate – gyrolite – begins to form (according to stoichiometry of this compound, the C/S molar ratio is equal to 0.66). Thermal conversions characteristic of this compound were identified in the DSC curve: endothermic (at 148 °C) and exothermic

(at 793 °C) (Fig. 3a). Presumably, one of the reasons for this is that the less active CaO is less soluble in water, moreover, that the water solubility of CaO, upon raising the temperature from 20 °C to 175 °C, decreases from 1.58 g/dm^3 to 0.17 g/dm^3 [21]. The larger amount of impurities and a smaller surface area of CaO change the time of lime slaking and thus influence the formation of calcium silicate hydrates. This means that the molar ratio of the reacting mixture is lower than in the raw materials, i.e. intermediate between 0.66 and 0.83, and there occur favourable conditions for the simultaneous crystallisation of the two compounds – gyrolite and 1.13 nm tobermorite.

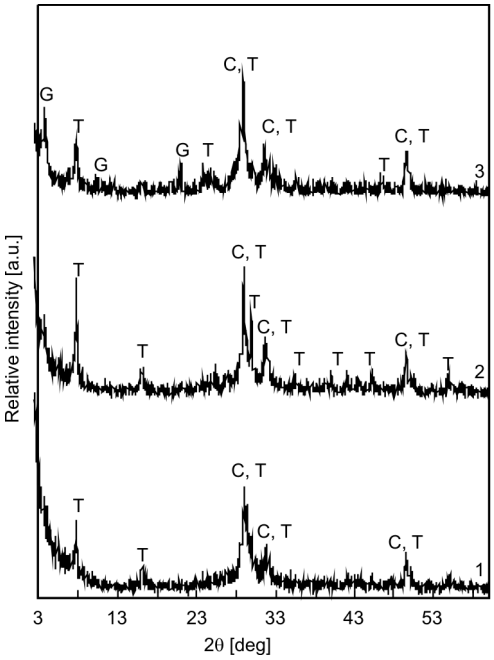

Fig. 2. X-ray diffraction patterns of the products of the synthesis; the C/S molar ratio is equal to 0.83 (less reactive CaO). Duration [h] of hydrothermal syntheses at 175 °C: 1 – 8; 2 – 24; 3 – 72; C – C–S–H (I), T – 1.13 nm tobermorite, G – gyrolite

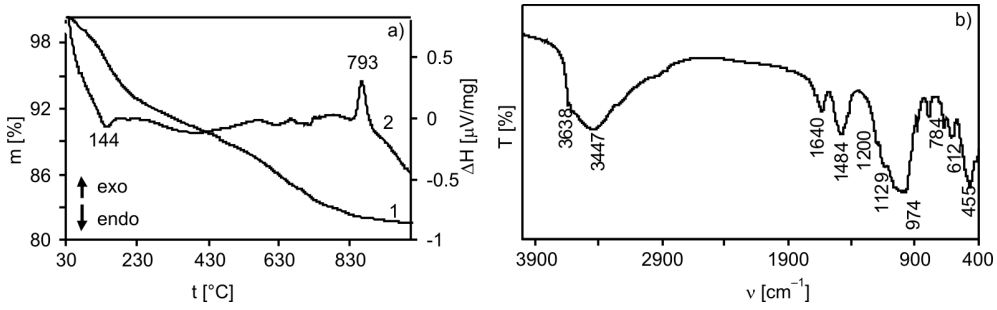

Fig. 3. STA curve (TGA – 1, DSC – 2) (a) and FTIR spectrum (b) of the products of the 72 h hydrothermal synthesis at 175 °C; the C/S molar ratio is equal to 0.83 (less reactive CaO)

All these results were confirmed by FTIR spectroscopy data, which can be used to distinguish gyrolite from other calcium silicate hydrates [22]. A sharp peak near

3635 cm^{-1} is visible only in the gyrolite spectrum (Fig. 3b). This clear band (3638 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. A wide band near 3447 cm^{-1} means the opposite – that molecular water forms hydrogen bridge links in the interlayers. The bands in the 1640 cm^{-1} frequency range are assigned to $\delta(H_2O)$ vibrations and confirm this presumption. Thus, the sequence of the formation of calcium silicate hydrates is highly dependent on the reactivity of the initial materials used for the preparation of the mixture – in this case, on the purity of CaO. It was found that in the mixtures with C/S = 0.83, the stoichiometric factor of products of the synthesis varies from 0.66 to 0.83 and depends on the CaO reactivity.

In order to evaluate the influence of higher CaO reactivity on the mixtures of higher basicity, i. e. with C/S = 1.0, similar hydrothermal syntheses were carried out. It was found that the reactivity of CaO has by far a great effect on the formation of monobasic calcium silicate hydrate. During the first 8 h of the synthesis, regardless of the CaO reactivity, a semicrystalline calcium silicate hydrate C–S–H (I) is formed (Fig. 4, curve 1, Fig. 6, curve 1).

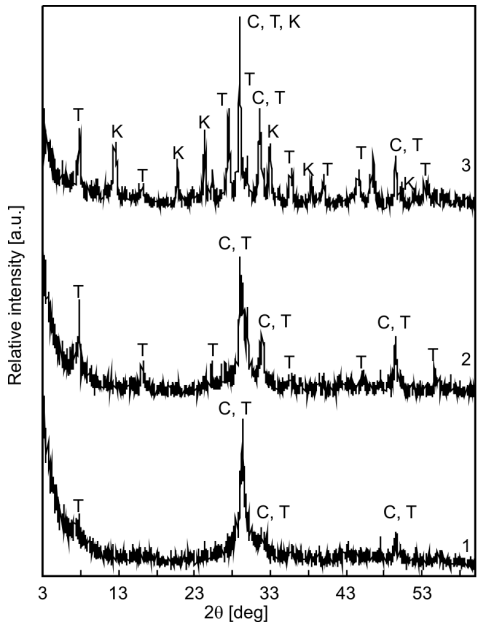

Fig. 4. X-ray diffraction patterns of the products of the synthesis; the C/S molar ratio is equal to 1.0. Duration [h] of hydrothermal syntheses at 175 °C: 1 – 8; 2 – 24; 3 – 72; C – C–S–H (I), T – 1.13 nm tobermorite, K – xonotlite

However, after 24 h of isothermal curing by using less reactive CaO, X-ray diffraction analysis curves showed only traces of 1.13 nm tobermorite (Fig. 6, curve 2), but if more reactive CaO is added to the initial mixture, 1.13 tobermorite having a noticeably higher degree of crystallization is formed (Fig. 4, curve 2). When the duration of the synthesis is prolonged even more, the effect of CaO reactivity on the composition of the product becomes even more obvious. When CaO of the lower reactivity is used in primary mixtures, 1.13 nm tobermorite and traces of gyrolite are formed

(Fig. 6, curve 3). The thermal conversion characteristic of gyrolite was identified in the DSC curve as an endothermic peak at 144 °C and an exothermic peak at 793 °C (Fig. 7a, curve 2). FTIR spectroscopy data supports the DSC results (Fig. 7b). It should be noted that typical peaks characteristic of xonotlite have not been identified in the X-ray diffraction analysis curves, even though the molar ratio C/S = 1.0 of the initial mixture corresponded specifically to the stoichiometric composition of this compound. In the mixture with more reactive CaO, both compounds – 1.13 nm tobermorite and xonotlite – are already formed after 72 h of synthesis (Fig. 4, curve 3). Thermal conversions characteristic of 1.13 nm tobermorite were identified in the DSC curve as an endothermic peak at 220 °C (Fig. 5a, curve 1).

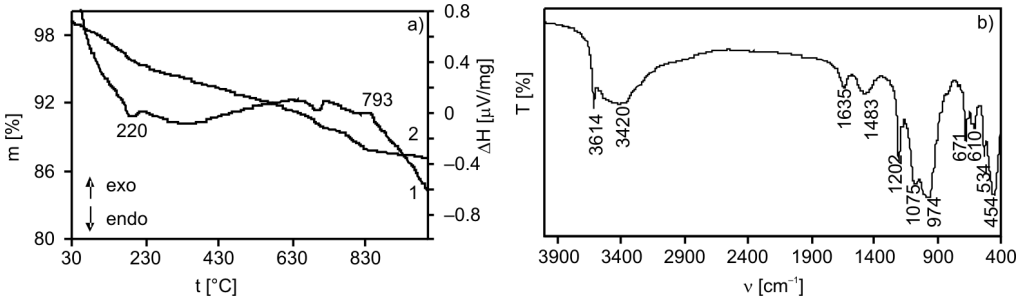

Fig. 5. STA curve (1 – DSC, 2 – TGA) (a) and FTIR spectrum (b) of the products of the 72 h hydrothermal synthesis at 175 °C when the C/S molar ratio is equal to 1.0

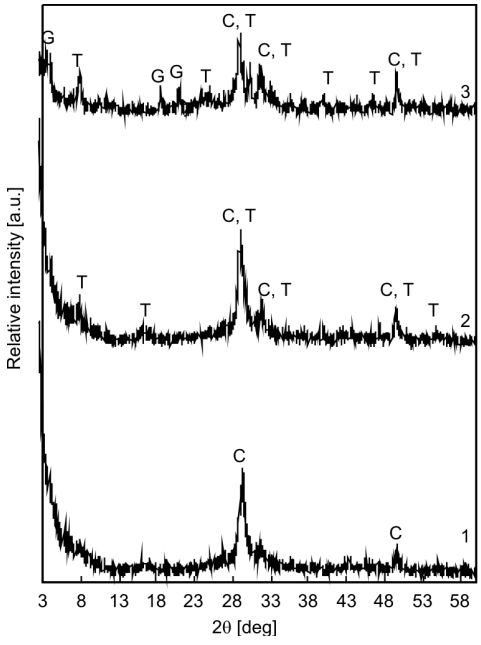

Fig. 6. X-ray diffraction patterns of the products of the synthesis; the C/S molar ratio is equal to 1.0 (less reactive CaO). Duration [h] of hydrothermal syntheses at 175 °C: 1 – 8; 2 – 24; 3 – 72; C – C–S–H (I), T – 1.13 nm tobermorite, G – gyrolite

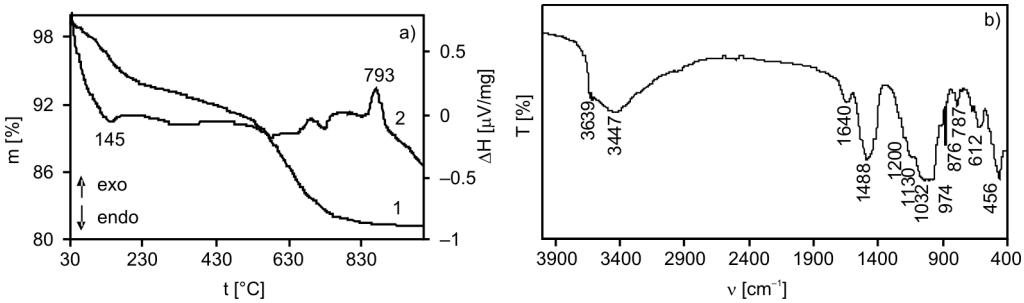

Fig. 7. STA curve (1 – DSC, 2 – TGA) (a) and FTIR spectrum (b) of the products of the 72 h hydrothermal synthesis at 175 °C when C/S molar ratio is equal to 1.0 (less reactive CaO)

Data that can be used to distinguish xonotlite from other calcium silicate hydrates [22] were confirmed by FTIR spectroscopy results: sharp peaks near 3614 cm^{-1} and near 1202 cm^{-1} are visible only in the xonotlite spectrum (Fig. 5b). Thus, when in the initial mixture the C/S molar ratio is equal to 1.0, CaO reactivity has a significant effect on the composition of products forming in hydrothermal conditions.

Thus the formation of calcium silicate hydrates proceeds during the reaction $CaO + SiO_2 \cdot nH_2O + H_2O$ under the outer surface of the particles of reagents. According to kinetic theory with influence of diffusion, when the crystallization products react at the outer surface of particles, the apparent order of reaction n is close to zero:

$$w_{app} = \frac{dx_{CaO}}{d\tau} = k_{app} F_R \left(\frac{dx}{dl}\right)^n$$

where w_{app} is the rate of reaction, k_{app} – a constant of apparent reaction, F_r – reactive surface of CaO, dx/dl – gradient of reagent concentration, n – apparent order of reaction.

$$\left(\begin{array}{c}\text{Particle of CaO}\\ O_{Fr}\end{array}\right) \xrightarrow{\tau,\ t, p, SiO_2 \cdot nH_2O} \text{C–S–H} \left(\begin{array}{l}\text{the former calcium silicate hydrate}\\ \text{composition depends}\\ \text{on the conditions of synthesis}\end{array}\right)$$

$$\downarrow$$

$$n \to 0$$

$$\left(\frac{dx}{dl}\right) \to 1;$$

$$w_{app.} = f(F_r)$$

It is obvious that the outer surface area of particles increases when the particles are milled. In this case, the apparent order of reaction increases as well. Therefore, the

factor limiting the formation of calcium silicate hydrate is the outer surface area F_r of calcium oxide particles.

It should be underlined that extra admixtures in the calcium oxide composition may have extra influence on the formation of products.

4. Conclusions

The reactivity of CaO changes the composition of intermediate and final products of the synthesis. In a pure Ca O–SiO_2·$n$$H_2O$–$H_2O$ system with CaO/SiO_2 = 0.83, the C–S–H (I) which forms at the beginning of synthesis is rather stable, and at 175 °C, even after 72 h, it only partially recrystallizes into 1.13 nm tobermorite. In the mixtures with less reactive CaO (96%), however, the stoichiometric composition of products of the syntheses varies from 0.66 to 0.83 because, together with 1.13 nm tobermorite, a low-base calcium silicate hydrate – gyrolite – begins forming.

When the CaO/SiO_2 molar ratio in the initial mixture is equal to 1.0, CaO reactivity has a significant influence on the composition of products forming in hydrothermal conditions. In the CaO–SiO_2·$n$$H_2O$–$H_2O$ system, after 72 h of synthesis at 175 °C in the mixture with more reactive CaO both compounds – 1.13 nm tobermorite and xonotlite – are formed. However, when the lower reactivity CaO is used in primary mixtures, only 1.13 nm tobermorite and traces of gyrolite are formed.

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