α-C₂SΗ synthesis in the mixtures with CaO/SiO₂=1.5 and application as a precursor for binder material

K. Baltakys, T. Dambrauskas*, A. Eisinas and R. Siauciuunas

Department of Silicate Technology, Kaunas University of Technology, Radiomen 19, LT-50270 Kaunas, Lithuania.

Received 22 September 2015; received in revised form 19 July 2016; accepted 5 November 2016

KEYWORDS
α-C₂S hydrate; Calcium silicate hydrate (C-S-H); Hydrothermal synthesis; Kilnoanite; Binder material.

Abstract. The parameters of α-C₂SΗ hydrothermal synthesis (4-72 h; 200°C) from a non-stoichiometric composition (CaO/SiO₂ = 1.5) of CaO and SiO₂·nH₂O mixture were determined, and a sequence of intermediary compound formation was examined and explained. It was estimated that in the synthesis products, α-C₂SΗ dominates at 200°C after 8 to 24 h. When duration of hydrothermal treatment was shorter - C-S-H(I) and C-S-H(II), as longer - kilnoanite, prevail in the products. Also, the hydration and strength properties of the binder material created on α-C₂SΗ basis were determined. The binder material was prepared by mixing α-C₂SΗ and quartz sand (1:1 by mass). Later on, sample was ground at 950 rpm for 4 min and burned at 450°C for 30 min under air atmosphere. It was determined that calorimetric curve of created binder material differs from the one of ordinary cements as it involves only the three exothermic reactions and the amount of total cumulative heat grows with the increasing hydration time. As expected, the tendency of strength increment was observed after 7-28 days of hardening: Compressive strength increased to 15.5 and 24.0 MPa, respectively. The products of synthesis and hardening were characterized by XRD, FT-IR, and STA analyses.

© 2016 Sharif University of Technology. All rights reserved.

1. Introduction

Calcium Silicate Hydrates (C-S-H) can be produced either by air curing, e.g. in cement (concrete), or hydrothermally by high pressure steam treatment in an autoclave. The production processes for fiber cement, calcium silicate boards, and autoclaved aerated concrete cover the whole range of calcium silicate hydrates from poorly crystallized to well crystallized. Hydration products of Portland cement are primary calcium silicate hydrate gels, which are a mixture of poorly crystallized particles. C-S-H has a wide compositional range, with molar CaO/SiO₂ (C/S) ratios between 0.6 and more than 2. The reaction pathway 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 [1-5]. The synthesis, properties, and structures of the compounds with molar ratio C/S = 0.8 – 1.0 (1.13 nm tobermorite, xonotlite) have been analyzed in detail [6-13].

Recently, synthesis, properties, and structures of α-C₂SΗ hydrate (α-C₂SΗ), a mostly common compound formed during a hardening of autoclaved calcium silicate products, have obtained a new interest, because on its basis, a new hydraulic cementitious materials family has been created [14,15]. The main feature of alternative hydraulic cementitious binder materials is the production in a two-step process:

1. Hydrothermal preparation of the calcium silicate hydrates in an autoclave with CaO/SiO₂ ratio from 1.25 to 2.0;

* Corresponding author. Tel: +370 7 300150; Fax: +370 7 300152; E-mail address: tadas.dambrauskas@ktu.lt (T. Dambrauskas)
2. Mechanochemical or thermal treatment of the hydrothermal products together with siliceous raw materials like sand, blast-furnace slag, glass, etc. or silica (usually 1:1).

Unlike ordinary Portland cement, the C-S-H phase is formed during the production of the binder and not during the hardening of concrete [15]. Initial tests showed its high chemical resistance and low carbonation rate due to low porosity [14], and its other important properties are similar to those of OPC. In particular, a monophasic hydraulic binder is provided based on silicate and a mixture containing this binder, which, as compared to conventional Portland cement and to hydraulic or latent hydraulic binders, respectively, lowers the energy consumption during binder manufacturing (manufactured at low temperatures) and the amount of the CO2 emissions, which show, using this binder, a lower total release or a more uniform release of heat during hydration and achieve higher durability and strength of building materials, respectively [15].

Many studies have been carried out regarding the synthesis of α-C2SH [16–19]. Synthesis is also possible from lime and quartz [17,20] or from lime and colloidal silica [21]. Hong and Glasser (2004) [22] constructed phase relations in the lime-rich (> 50% Ca(OH)2) portion of the CaO-SiO2-H2O system at saturated steam pressures (Ca/Si=0.83–3.0; 55–220°C; 360 days). It should be underlined that α-C2SH is formed always with portlandite. According to several sources [23,24], α-C2SH forms quite easily under hydrothermal conditions from CaO and silicic acid as the starting materials in the temperature range 150–200°C.

Hu et al. (2006) [25] determined that α-C2SH is stable at low temperatures and starts to decompose at 180°C to form Ca-rich jahfeite, and finally form dellite at 350°C for 8 days. Hillebrandite was a stable phase at temperatures lower than 350°C, but was transformed directly to dellite at temperatures higher than 350°C within 1–2 days. Detellite was reversibly transformed to hillebrandite at lower temperatures below 300°C with formation of a small amount of the C-S-H compounds with C/S ratio of 1.5. Meanwhile, hillebrandite is stable only over a short range of temperature between 160 and 210°C and at higher temperature; it decomposes to α-C2SH and portlandite after a very long-term hydrothermal treatment, when reactions of intermediary compound formation are completed [22].

Thus, there is little data (not comprehensive) in the references concerning the synthesis of α-C2SH and the sequence of the new compounds formed in the CaO-amorphous SiO2-H2O mixture.

The main objective of the present work is to determine the parameters of α-C2SH hydrothermal synthesis as well as to analyze and explain the sequence of intermediary compound formation. The hydration and strength properties of the binder material created on α-C2SH basis are highlighted.

2. Materials and methods

2.1. Materials

In this paper, the following reagents were used: SiO2-nH2O ("Reaktiv", Russia) was grounded for 2.5 min in a vibrating cup “Pulverisette 9” mill (speed: 850 rpm) and sieved through a sieve with a mesh size of 80 μm; S4 = 1291 m²/kg by CILAS LD 1000 granulometer; and the loss of ignition: -5.19 wt.%. Calcium oxide from Ca(OH)2 (“Reaktiv", Russia) was additionally burned at 550°C temperature for 1 h, grounded for 30 s in a vibrating cup “Pulverisette 9” mill (speed: 600 rpm), and sieved through a sieve with a mesh size of 80 μm. The quantity of free CaO is equal to 98.7 wt.%. Quartz sand ("Anykslis kvarcias", Lithuania, S6 = 28.7 m²/kg) was sieved through a sieve with a mesh width of 400 μm. The chemical analysis of quartz sand is shown in Table 1.

2.2. Hydrothermal synthesis of α-C2SH

Dry primary mixture with C/S molar ratio of 1.5 was mixed with water to reach the water/solid ratio of the suspension equal to 10:1. The hydrothermal synthesis has been carried out in unsterilized suspensions in 25 ml volume PTFE cells, which were placed in “Parr instruments” (Germany) autoclave under saturated steam pressure in argon atmosphere at 200°C temperature for 8, 16, 24, 48, and 72 hours by applying extra argon gas (10 bar). 200°C temperature was reached within 2 h. After hydrothermal treatments, the autoclave was quenched to room temperature. The suspensions after synthesis were filtered, and the pH values of liquid phase (~ 15 ml) were measured by a Mettler Toledo T70 pH meter at room temperature. Synthesis products were rinsed with acetone to prevent carbonization of materials, dried at 50°C ± 5 temperatures for 24 h, and sieved through a sieve with a size width of 80 μm.

2.3. Manufacture of binder material

The Binder Material (BM) was prepared by mixing α-C2SH (C/S = 1.5; 16 h, 200°C) with quartz sand (1:1 by mass) in a homogenizer (Turbula) at 34 rpm for

---

**Table 1. Chemical composition of quartz sand.**

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO2</th>
<th>P2O5</th>
<th>CaO</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount (%)</td>
<td>98.3</td>
<td>0.81</td>
<td>0.30</td>
<td>0.09</td>
<td>0.06</td>
<td>0.44</td>
</tr>
</tbody>
</table>

---

K. Baltaks et al. / Scientia Iranica, Transactions C: Chemistry and ... 23 (2016) 2800–2810 2801
30 min. Later on, BM sample was ground in a vibrating cup mill (“Pulverisette 9”) at 950 rpm for 4 min and burned at 450°C for 30 min. According to the results of particle size analysis, after 4 min interaction, the diameter of particles varied from 0.03 to 82 μm. In addition, two fraction particles, with an average sizes of 1.4 and 22 μm, were dominated in the BM sample.

2.4. Isothermal calorimetry

An eight channel TAM Air III isothermal calorimeter was used to investigate the heat evolution rate of the BM. Glass ampoules (20 ml), each containing 3g dry cementitious material, were placed in the calorimeter and the injection units for each ampoule were filled with amounts of water equivalent to a W/MB ratio of 0.5. After a steady temperature of 25°C was reached, the water was injected into the ampoules and mixed inside the calorimeter with the dry material for 20 s (frequency 2-3 s⁻¹). The heat evolution rate was then measured over a period of 72 h. Repetition of the measurements showed deviations in total heat below 3% for samples of similar type. Apart from the first minutes of water additive and mixing, the heat evolution rates were essentially identical.

2.5. Compressive strength and mineralogical analyses of BM samples

To make a more exact estimation of the hydration process, the samples (20 × 20 × 20 mm) for instrumental analysis and compressive strength were usually prepared without sand according to requirements of LST EN 196-1 ± 3 standards. Samples were formed from the BM when the ratio of water to BM was equal to 0.35. During the first day, the samples were kept in molds at 20 ± 1°C and 100% humidity. After 24 h of formation, the samples were transferred into distilled water and stored there for 2, 6, 13, and 27 days at 20±1°C. Hydration of samples was stopped by acetone.

The data of compressive strength test were calculated as the arithmetic mean of the six individual results. The samples (for instrumental analysis) were crushed to powder, dried at the temperature of 50 ± 5°C, and sieved through a sieve with a mesh width of 80 μm.

2.6. Analytical techniques

The X-Ray powder Diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu Kα radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2θ = 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 samples 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. Calibration of temperature and enthalpy was carried out by TGA/DSC calibration kit in the temperature ranging from RT to 900°C, consisting of 8 samples and following the instrument supplier instructions, ASTM E 968:2008.

FT-IR spectra have been carried out with the help of a Perkin Elmer FT-IR 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 spectral resolution of 1 cm⁻¹.

Compressive strength of the samples was performed with “ELE International 250 kN Automatic Cement Compression Machine, EL39-1501/01 Autotest250” press. The data of compressive strength test were calculated as the arithmetic mean of the three individual results.

The particle size distribution was measured using a CILAS 1000 LD grain-size analyzer, which has a sensitivity range from 0.04 to 500 μm. The particles were dispersed by ultrasound for 2 min while the obscuration of particles in water reached 14%. The ultrasound duration during the measurement was 70 s. The standard operating procedure used was the Fraunhofer method.

3. Results and discussions

3.1. Hydrothermal synthesis of α-C₂S₉H

It was determined that in unstirred CaO-SiO₂-nH₂O-H₂O suspensions when the molar ratio (CaO/SiO₂) of primary mixture was equal to 1.5, within 4 hours of isothermal curing at 200°C, partially reacted portlandite (d-spacing=0.493, 0.362, 0.193 nm), α-C₂S₉H (2CaO.SiO₂.H₂O; d-spacing=0.422, 0.326, 0.266, 0.241 nm), and semi-crystalline C-S-H type compounds (d-spacing=0.303; 0.280; 0.184 nm) were formed in the products (Figure 1, curve 1). Moreover, the carbonation appeared when the products were dried in air conditioned chamber (50°C, 24 h) and a fair amount of CaCO₃ (d-spacing=0.304, 0.191 nm) was formed irrespective of synthesis duration. This was additionally confirmed by FT-IR and STA analyses.

In DSC curve, the first endothermic effect (30-210°C) can be assigned to dehydration of crystallization water in calcium silicate hydrates. The decomposition of portlandite is observed in the same temperature interval (400-500°C) as the dehydration of α-C₂S₉H. However, after 4 h of isothermal curing, the latter process was intensively proceeded in a wide temperature range, and it overlapped the endothermic effect typical for portlandite decomposition (Figure 2,
It should be noted that only one endothermic effect is observed in the derivation of DSC curve (Figure 2, curve 3). For this reason, it is impossible to separate these two thermal conversions. It was calculated that, above 800°C, during the recrystallization of semi-crystalline C-S-H-type compounds (C-S-H(I) and C-S-H(II), respectively) to wollastonite, the quantity of the heat flow is equal to 1.53 J/g, for C-S-H(I), and 5.61 J/g, for C-S-H(II) (Figure 2, curves 2 and 3, Table 2). Furthermore, an endothermic effect at ~714°C can be assigned to the decomposition of calcium carbonate (Figure 2, curve 2). According to TGA analysis data, it was calculated that 8% of the latter compound is present in the synthesis products (Figure 2, curve 1).

Within 8 h of hydrothermal synthesis, Ca(OH)₂ was fully reacted, because there was no evidence of characteristics of diffraction peaks for this compound in the XRD patterns (Figure 1, curve 2). In previous works [26,27], the same tendency was observed, when the duration of hydrothermal synthesis at 175°C temperature was 16 hours.

Moreover, in comparison with 4 h of isothermal curing, the intensity of α-C₂SH diffraction peaks increased several times (Figure 1, curves 1 and 2) and its heat flow of dehydration was equal to 58.55 J/g (Figure 3, curve 2, Table 2). The dehydration of α-C₂SH proceeded at 400-500°C; according to the reaction: α-2CaO·SiO₂·H₂O→2CaO·SiO₂ + H₂O, the mass loss of the mentioned compound was equal to 4.45 wt.%, resulting in 48.95% of formed α-C₂SH (Table 3). It should be underlined that this value is in good agreement with the data obtained by Ishida et al. (1993) [23].

It was determined that by prolonging the duration of hydrothermal synthesis to 16 h, the intensity of diffraction maximums specific to α-C₂SH was increased (Figure 1, curve 3). Also, the diffraction peaks, which

---

**Figure 1.** XRD patterns of the synthesized products in the mixtures with C/S molar ratio of 1.5, when the duration of hydrothermal treatment at 200°C temperature is h: 1-4; 2-8; 3-16; 4-72. Indexes: α-C-S-H; α=α-C₂SH; p=Ca(OH)₂; d-kaolinite; k=CaCO₃.

**Figure 2.** TGA (curve 1), DSC (curve 2), and DDSC (curve 3) curves of the synthesized product, when the duration of hydrothermal treatment at 200°C temperature is 4 h.
Table 2. Dependence of pH value of medium and the heat of thermal effects typical for α-C2SH, C-S-H(I) and C-S-H(II) on duration of synthesis.

<table>
<thead>
<tr>
<th>Hydrothermal synthesis duration, h, at 200°C temperature*</th>
<th>pH value of medium</th>
<th>Heat of thermal effect (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature range (°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α-C2SH</td>
</tr>
<tr>
<td>4</td>
<td>12.39</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>12.37</td>
<td>58.55</td>
</tr>
<tr>
<td>16</td>
<td>12.25</td>
<td>94.03</td>
</tr>
<tr>
<td>24</td>
<td>12.15</td>
<td>16.97</td>
</tr>
<tr>
<td>72</td>
<td>11.90</td>
<td>—</td>
</tr>
</tbody>
</table>

*: The molar C/S ratio of dry primary mixture was equal to 1.5 and water/solid ratio of the suspension was equal to 10.0.

Table 3. The quantity of α-C2SH and CaCO3 in the synthesis products.

<table>
<thead>
<tr>
<th>Hydrothermal synthesis duration, h, at 200°C temperature*</th>
<th>Mass losses at 400-500°C (%)</th>
<th>Quantity (%)</th>
<th>Mass losses at 650-750°C (%)</th>
<th>Quantity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-C2SH</td>
<td>C-S-H(I)</td>
<td>C-S-H(II)</td>
<td>α-C2SH</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>4.45</td>
<td>48.95</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>4.37</td>
<td>48.07</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>24</td>
<td>1.96</td>
<td>21.36</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>72</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*: The molar C/S ratio of dry primary mixture was equal to 1.5 and water/solid ratio of the suspension was equal to 10.0.

Figure 3. TGA (curve 1), DSC (curve 2), and DDSC (curve 3) curves of the synthesized product, when the duration of hydrothermal treatment at 200°C temperature is 8 h.

*d-spacing is 0.533 nm from planes (002) and 0.266 nm from planes (004), are more intensive and can be associated with the beginning of α-C2SH recrystallization (Figure 1, curve 3). DSC data confirmed that a larger amount of the main synthesized product, α-C2SH, is formed due to the observed increase in the dehydration heat flow (in 1.6 times). It was estimated that after 8-16 h of synthesis, about 48-50% of α-C2SH was formed (Table 3).

Unexpected results were obtained after 24 h of hydrothermal treatment; a recrystallization of α-C2SH to kilekoanite (d-spacing 0.355; 0.304; 0.288; 0.267).
which is not consisted of water (Ca$_6$(SiO$_4$)(Si$_9$O$_{26}$)), was observed. XRD data were supported by STA analysis results. In DSC curve, an endothermic effect, reflecting the removal of crystallization water, was not observed in 70-150°C temperatures interval (Figure 4, curve 1). Meanwhile, the heat flow of α-C$_2$SH dehydration decreased from 94.03 J/g to 16.97 J/g (Table 2) although the latter compound was not identified in the XRD patterns. It should be underlined that in the synthesis products, the amount of calcium carbonate decreased (2.9 wt.%) too. This fact can be explained by the kihloconite resistance to carbonization. Moreover, an exothermic effect typical for C-S-H(I) recrystallization in other compounds was not identified.

The present results are in good agreement with the data obtained by Black et al. (2003) [28]. It was determined that during hydrothermal synthesis of α-C$_2$SH at 200°C, kihloconite was also formed in the products. In this case, α-C$_2$SH was prepared from β-C$_2$S which was treated mechanochemically in an agate ball mill for 24 h and followed by hydrothermal treatment. The same tendency was observed in N. Meller et al. (2009) [29] work, in which the hydrothermal reactions of an oil well cement with added silica and alumina, during hydration (200 to 350°C), were examined, and it was estimated that kihloconite was formed in the samples at 200°C.

Remarkable changes were noticed in the FT-IR spectrum of synthesis products (Figure 5). The significant increase in the intensity of absorption bands attributed to OH$^-$ and H$_2$O vibrations was observed. The assumption that the structure of kihloconite does not contain any water was proven by the low intensity absorption maximums at $\sim$ 1620 and $\sim$ 3482 cm$^{-1}$. In bending $\delta$(Si-O-Si) and $\delta$(O-Si-O) vibrations range, two absorption bands at $\sim$ 434, $\sim$ 583 cm$^{-1}$ and the doubllet at $\sim$ 495, $\sim$ 516 cm$^{-1}$ were identified. Meanwhile, a triplet at $\sim$ 896, $\sim$ 930, $\sim$ 977 cm$^{-1}$, which can be attributed to symmetrical $\nu_s$(O-Si-O) stretching signals, was observed. Two absorption bands assigned to asymmetrical $\nu_{as}$ (Si-O-Si) stretching vibrations were identified at $\sim$ 1045 cm$^{-1}$; the latter one shows that [SiO$_4$]$^{4-}$ tetrahedron forms a triple chain in the structure of synthesis products. It should be noted that a significant increase in the intensity of absorption signal at $\sim$ 710 cm$^{-1}$ was also observed, reflecting the symmetrical $\nu_s$(Si-O-Si) stretching vibrations. Moreover, the absorption maximum at $\sim$ 1282 cm$^{-1}$ can be assigned to bending $\delta$(OH(Si)) signals.

Furthermore, after extending the duration of isothermal curing to 48 and 72 h, α-C$_2$SH was fully recrystallized to kihloconite due to undetected diffraction maximums specific to α-C$_2$SH in XRD patterns (Figure 1, curve 4). Also, an endothermic effect at $\sim$ 460°C temperature, which can be assigned to the latter compound, is not visible (Figure 6). Furthermore, thermal conversions attributed to kihloconite as well as the removal of crystallization water are not observed in DSC curves. $\sim$ 0.8% of mass losses estimated in 80-150°C temperature range can be ascribed to the dehydration of C-S-H(I) (Figure 6, curve 1). No visible
changes appeared in FT-IR spectrum; only absorption band, reflecting bending $\delta$(H$_2$O) vibrations, shifted to a lower frequency range, that is, it was observed at 1592 cm$^{-1}$.

It is possible to assume that when curing the mixture of CaO and amorphous SiO$_2$ at 200°C temperature under the saturated steam pressure, the reactions of a new compounds formation occur in the following sequence:

$$1.5\text{CaO} + \text{SiO}_2\cdot n\text{H}_2\text{O} + 10\text{H}_2\text{O} \xrightarrow{4\text{h}} \text{C-S-H(I)}$$

$$\xrightarrow{8\text{h}} \begin{align*}
\text{C-S-H(II)} & \quad \text{CaCO}_3 \\
\text{CaCO}_3 & \quad \text{kilchoanite}
\end{align*}$$

$$\xrightarrow{24\text{h}} \begin{align*}
\text{C-S-H(I)} & \quad \text{CaCO}_3 \\
\text{caCO}_3 & \quad \text{kilchoanite}
\end{align*}$$

Thus, $\alpha$-C$_2$S hydrate can be synthesized from a non-stoichiometric composition (the molar ratio $C/S = 1.5$) of CaO and SiO$_2$, $n$H$_2$O in unstirred suspensions. $\alpha$-C$_2$SH without impurities of portlandite is formed after 8 h at 200°C. It starts to recrystallize into kilchoanite (with molar ratio being equal to 1.5) after 24 h of treatment. In the second part of the work, the synthesized $\alpha$-C$_2$SH was used to prepare some hydraulic cementsitious materials.

### 3.2. Hydration properties of BM

It is known that conventional hydraulic binders based on silicates do not contain any molecular water; their hydraulic components contain no hydrogen in their chemical composition, and the hydraulic components for the most part consist of crystalline alkali (earth) silicates. In a case of the alternative binder material based on $\alpha$-C$_2$SH, the product of hydrothermal synthesis does not exhibit hydraulic activity, because it is stabilized by hydrogen bonds in which silanol groups are involved.

In order to achieve hydraulic activity, the mixture of this product must be activated tribochemically with another inert component containing SiO$_2$, such as quartz, and subsequently treated thermally. In this case, mentioned hydrogen bonds are destroyed, and reactive fragments are deposited in a dispersed state on the silicate surfaces [15].

For these reasons, the Binder Material (BM) was prepared by mixing $\alpha$-C$_2$SH ($C/S = 1.5$; 16 h, 200°C) and quartz sand (1:1 by mass) in a homogeniser (Turbula) at 34 rpm for 30 min. Later on, BM sample was ground in a vibrating cup mill ("Pulverisette 9") at 950 rpm for 4 min. It was determined that after grinding, the BM sample was significantly amorphized. This fact was confirmed by XRD analysis: the intensity of diffraction peaks specific to $\alpha$-C$_2$SH ($d$-spacing 0.422; 0.327; 0.266; 0.241 nm) and quartz ($d$-spacing 0.426; 0.335; 0.247 nm) decreased (Figure 7(a), curve 2); a plot area of endothermic effect at 480°C temperature on the DSC curve (Figure 7(b), curve 2) decreased. It is
known [30] that the amount of decomposed $\alpha$-C$_2$SH during the grinding has a substantial effect on the hydration properties and strength development of the binder material. Due to the fact that during hydration, the reactive components are formed from $\alpha$-C$_2$SH, BM samples were burned at 450°C for 30 min under air atmosphere. As it was expected, after calcination, the complete destruction of $\alpha$-C$_2$SH proceeded because in XRD pattern, the diffraction peaks with $d$-spacing 0.422, 0.327, 0.266, 0.241 nm were not identified (Figure 9, curve 1).

Data on the rates of heat evolution (W/g) of BM are presented in Figure 8. It was determined that calorimetric curve of BM differs from the one with ordinary cements as it involves only the three exothermic reactions (Figure 8(a)). In the first exothermic reactions, there is a rapid evolution of the heat culminating in a peak within the first 1-2 min. And, the heat flow is equal to 0.0036 W/g. This is ascribed to the effects of the heat of wetting of BM.

The next peaks are primarily associated with heat released due to hydration reactions (Reaction 1). Meanwhile, the second exothermic reaction proceeds from 0.2 h to 0.5 h (Figure 8(a), point 2), and the total heat of process increases to 2.85 J/g (Figure 8(b)). The maximum cumulative heat (39.75 J/g) was released by the third exothermic reaction which occurs between 3 and 18 h (Figure 7(a)).

At later stages of hydration, the calorimetric curve of BM shows the slow continuous reaction because the rate of heat evolution decreases. Meanwhile, the amount of total cumulative heat grows with the increasing hydration time (Figure 8(b)).

The fundamental process of chemical hydration reactions between BM and water after wetting process (2 and 3 exothermic reactions) can be described by this hypothetical reaction:

$$C_{1.5}S_1 + xQ + H_2O \rightarrow C_{1.5}S_{(1+y)}H + (x-y)Q + \Delta H,$$

where $C_{1.5}S_1$ is the compound formed after grinding and burning; $Q$ is quartz; $C_{1.5}S_{(1+y)}H$ is the compound formed after hydration; $\Delta H$ is heat; $x$ is molar content of quartz in binding material; and $y$ is molar content of reacted quartz in hydrated cement stone.

In order to prove the influence of hydration on crystalline phase quantity, the amount of quartz was determined in the hydration products. For this reason, the heat evolution experiments were repeated at different time intervals (1.8 h and 12 h) under normal conditions. Hydration of samples was stopped by using acetone. Later on, the samples were crushed to powder, dried at the temperature of 50 ± 5°C, and put through a sieve with an 80-μm mesh. Quartz quantity was calculated from the intensity change of the basic reflection (0.334 nm). Each calculation was done 5 times, and it was determined that their data declined no more than ±5% from the mean.

As results show in Figure 9, only 4-5% of quartz reacts during the first 1.8 hours and the further reduction of its quantity depends on duration of hydration, i.e., 25% of unreacted quartz remains in the BM sample after 12 h.

In order to evaluate the mechanical properties of the BM samples, the compressive strength properties were determined (Figure 10). After three days, hydration of the compressive strength of BM was equal to 6.7 MPa. As expected, the tendency of strength increment was observed after 7-28 days of hardening: Compressive strength increased to 15.5 and 24.0 MPa, respectively (Figure 10).

To explain the nature of the strength properties of samples, XRD and STA analyses of the hydrated products were carried out. In the XRD analysis curves, after 28 days of hydration, the peaks of calcium silicate hydrates ($d$-spacing: 0.303; 0.280; 0.184 nm) were observed (Figure 11(a)). It should be noted that the intensity of diffraction peaks ($d$-spacing: 0.426; 0.335; 0.182; 0.154 nm) specific to quartz and a low intensity diffraction peak specific to $\alpha$-C$_2$SH ($d$-spacing: 0.326; 0.266; 0.241 nm) were identified (Figure 11(a)).

XRD results were confirmed by DSC data. The
first endothermic peak at 50-150°C is the result of dehydration reactions due to the loss of water from C–S–H structure. The endothermic peak at 579°C shows the α-β transition of quartz. The exothermic peak (850°C) is associated with recrystallization of C–S–H into wollastonite (Figure 11(b)).

Thus, the mechanical properties are specific to the created binder material on α-C2SH basis. The results presented here show that the α-C2SH, after intensive grinding with quartz sand and burning, has strength features. For this reason, in the further research, in order to use created binder material based on synthetic α-C2SH as alternative cementitious material, the setting and hardening characteristics will be performed by making mortar and concrete.

4. Conclusions

1. When the molar ratio CaO/SiO2 of primary mixture was equal to 1.5, it was determined that in un-stirred CaO–SiO2, nH2O–H2O suspensions, within 4 hours of isothermal curing at 200°C, dicalcium silicate hydrates –α-C2SH, C-S-H(II) and a low base semi-crystalline C-S-H(I) type calcium silicate hydrate were formed. It was observed that Ca(OH)2 fully reacted to 8 h of synthesis, and α-C2SH is a domination mineral in the synthesis product after 16 h of curing.

2. At 200°C, after 24 h of hydrothermal treatment, α-C2SH starts to recrystallize into kilchoanite. Furthermore, after extending the duration of isothermal curing to 48 h, α-C2SH is fully recrystallized to kilchoanite.

3. It was estimated that the heat evolution and com-
pressive strength properties are characteristics of created binder material on α-C₂₃H₂₄O₇-quartz basis. It was determined that the calorimetric curve of BM involves the three exothermic reactions as the maximum cumulative heat (39.75 J/g) was released by the third exothermic reaction which occurs between 3 and 18 h. Also, the tendency of strength increment was observed after 7-28 days of hardening: compressive strength increased to 15.53 and 24.00 MPa, respectively.

Acknowledgement

This research was funded by a grant (No. MIP-025/2014) from the Research Council of Lithuania.

References


Biographies

**Kestutis Baltakis** is a Professor at the Department of Silicate Technology at Kaunas University of Technology, in Lithuania. He received his PhD degree in Chemical Engineering from Kaunas University of Technology at the age of 26. He is the author and co-author of more than 50 papers in ISI WOS list journals, a monograph, a textbook. He has been in France 2 times for internship and also participated in more than 35 international conferences. Professor Baltakis supervised 3 PhD students whose theses were defended. He accomplished over 10 ordered agriculture industry work agreements.

His research interests include the development of cement and related building materials properties. He also evaluated structure peculiarities of calcium silicate hydrates and application in the innovative technologies. Prof. Baltakis created the new generation purposeful silicate materials and their composites by using advanced synthesis methods. He explained and refined their crystal structures and proposed the new application areas by implementing many modern instrumental methods and analyses. Moreover, he performed the extensive theoretical and applied research works, and obtained the new results of investigative work, which still have a significant impact on the development of higher technologies and the creation of new innovative technologies.

**Tadas Dambrauskas** is a PhD student at the Department of Silicate Technology in Kaunas University of Technology, in Lithuania. He received his MS degree in Chemical Engineering from Kaunas University of Technology in 2015. His main research interests are the synthesis and functional properties of dibasic calcium silicate hydrates. He is author and co-author of 6 papers in ISI WOS list journals, patent of Lithuanian. Also, he has participated in 9 international conferences.

**Anatolijus Eisinas** is an Associate Professor at the Department of Silicate Technology in Kaunas University of Technology. He received his PhD degree in Chemical Engineering from Kaunas University of Technology at the age of 29. He is a co-author of 20 papers listed in ISI WOS journals and a textbook. He went to Latvia for internship several times; he participated in more than 15 international conferences and accomplished 4 agriculture industry work agreements. Dr. Eisinas is a member of qualifying board of bachelor studies of KTU Chemical Engineering field and has one PhD student.

His research interests are the synthesis, properties, and application of silicate materials. He developed a new generation specific to silicate materials and their composites by using advanced synthesis method, combining a number of modern instrumental methods of analysis results clarifying and revising its crystal structure and proposed new application scope.

**Raimundas Siauciuinas** is a Professor at the Department of Silicate Technology in Kaunas University of Technology. He received his PhD degree in Cement Chemistry and Technology Field from Riga Technical University (Latvia), in 1989. He is author and co-author of more than 140 scientific papers including 35 papers in Thomson Reuters WoK list journals, a monograph, and 5 textbooks. Dr. Siauciuinas is a member of Lithuanian Academy of Sciences and the Head of a Doctoral Committee in Chemical Engineering field at Kaunas University of Technology, where he supervised 5 PhD students whose projects were defended, and at this time he is the head of 3 PhD students. Dr. Siauciuinas has a good cooperation with Munich Technical University where his 15 students at level of PhD and Master Degrees were on internships.

The main research interests of Dr. Siauciuinas are the chemistry of cement and related building materials, particularly the synthesis, properties and application of calcium silicate hydrates. During the last 5 years, he was the head of 3 grants from Research Council of Lithuania, and participated in 15 international conferences.