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# $\alpha$-$C_2SH$ synthesis in the mixtures with $CaO/SiO_2$=1.5 and application as a precursor for binder material

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Hydrothermal synthesis;
Kilchoanite;
Binder material.

**Abstract.** The parameters of $\alpha$-$C_2SH$ hydrothermal synthesis (4-72 h; 200°C) from a non-stoichiometric composition ($CaO/SiO_2$ = 1.5) of CaO and $SiO_2.nH_2O$ mixture were determined, and a sequence of intermediary compound formation was examined and explained. It was estimated that in the synthesis products, $\alpha$-$C_2SH$ 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 - kilchoanite, prevail in the products. Also, the hydration and strength properties of the binder material created on $\alpha$-$C_2SH$ basis were determined. The binder material was prepared by mixing $\alpha$-$C_2SH$ 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.

## 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 $CaO/SiO_2$ ($C/S$) 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 $\alpha$-$C_2S$ hydrate ($\alpha$-$C_2SH$), 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 $CaO/SiO_2$ ratio from 1.25 to 2.0;

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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 mono-phase 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 $CO_2$ 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 $\alpha$-$C_2SH$ [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 $CaO$-$SiO_2$-$H_2O$ system at saturated steam pressures (Ca/Si=0.83-3.0; 55-220°C; 360 days). It should be underlined that $\alpha$-$C_2SH$ is formed always with portlandite. According to several sources [23,24], $\alpha$-$C_2SH$ 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 $\alpha$-$C_2SH$ is stable at low temperatures and starts to decompose at 180°C to form Ca-rich jaffeite, and finally form dellaite at 350°C for 8 days. Hillebrandite was a stable phase at temperatures lower than 350°C, but was transformed directly to dellaite at temperatures higher than 350°C within 1-2 days. Dellaite 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 $\alpha$-$C_2SH$ 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 $\alpha$-$C_2SH$ and the sequence of the new compounds formed in the CaO-amorphous $SiO_2$-$H_2O$ mixture.

The main objective of the present work is to determine the parameters of $\alpha$-$C_2SH$ 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 $\alpha$-$C_2SH$ basis are highlighted.

## 2. Materials and methods

### 2.1. Materials

In this paper, the following reagents were used: $SiO_2.nH_2O$ ("Reaktiv", Russia) was grinded 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; $S_a = 1291\ m^2/kg$ by CILAS LD 1090 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, grinded 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 ("Anyksciu kvarcas", Lithuania, $S_a = 28.7\ m^2/kg$) 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 $\alpha$-$C_2SH$

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 10.0. The hydrothermal synthesis has been carried out in unstirred 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 $\alpha$-$C_2SH$ ($C/S = 1.5$; 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.

| **Oxides** | **$SiO_2$** | **$P_2O_5$** | **CaO** | **$Al_2O_3$** | **$Fe_2O_3$** | **Other** |
|---|---|---|---|---|---|---|
| **Amount (%)** | 98.3 | 0.81 | 0.30 | 0.09 | 0.06 | 0.44 |

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 $\mu$m. In addition, two fraction particles, with an average sizes of 1.4 and 22 $\mu$m, 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/BM 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 $\mu$m.

### *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 K$\alpha$ radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2 - 60°$ ($2\theta$) in steps of $2\theta = 0.02°$.

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 Maschine, 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 1090 LD grain-size analyzer, which has a sensitivity range from 0.04 to 500 $\mu$m. 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 Fraunhöfer method.

## 3. Results and discussions

### *3.1. Hydrothermal synthesis of $\alpha$-$C_2SH$*

It was determined that in unstirred $CaO\text{-}SiO_2.nH_2O\text{-}H_2O$ suspensions when the molar ratio ($CaO/SiO_2$) of primary mixture was equal to 1.5, within 4 hours of isothermal curing at 200°C, partially unreacted portlandite (*d-spacing*-0.493, 0.262, 0.193 nm), $\alpha$-$C_2SH$ ($2CaO.SiO_2.H_2O$; *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 $CaCO_3$ (*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 $\alpha$-$C_2SH$. 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,

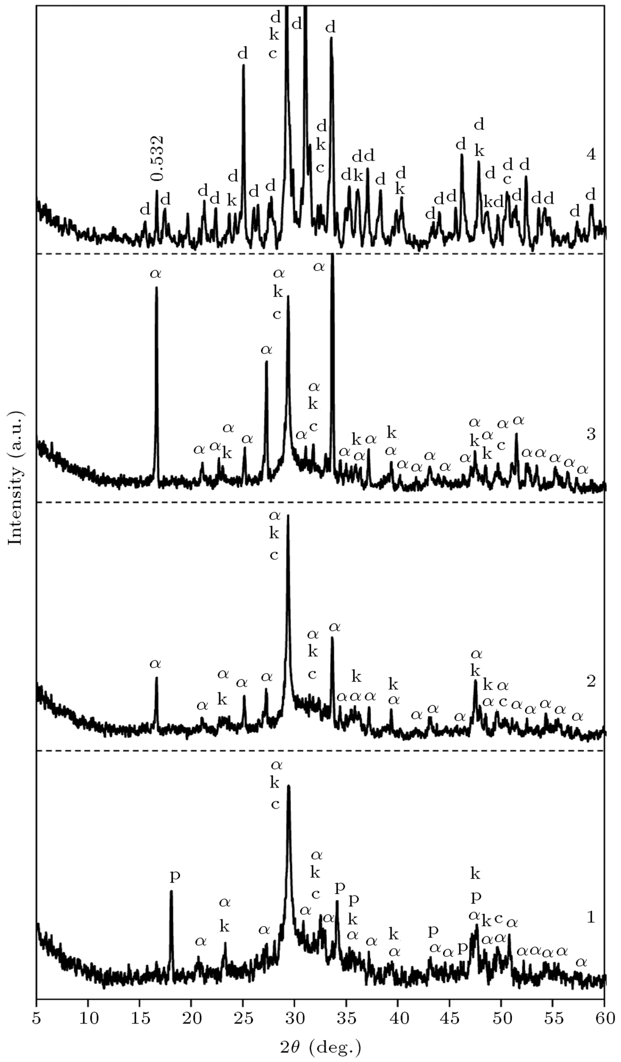


**Figure 1.** XRD patterns of the synthesized products in the mixtures with $C/S$ molar ratio of 1.5, when the duration of hydrothermal treatment at 200°C temperature is h: 1-4; 2-8; 3-16; 4-72. Indexes: c-C-S-H; $\alpha$–$\alpha$-$C_2SH$; $p$–$Ca(OH)_2$; $d$–kilchoanite; $k$–$CaCO_3$.

curve 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 $\alpha$-$C_2SH$ 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 $\alpha$-$C_2SH$ proceeded at 400-500°C; according to the reaction: $\alpha\text{-}2CaO.SiO_2.H_2O \rightarrow 2CaO.SiO_2 + H_2O$, the mass loss of the mentioned compound was equal to 4.45 wt.%, resulting in 48.95% of formed $\alpha$-$C_2SH$ (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 $\alpha$-$C_2SH$ was increased (Figure 1, curve 3). Also, the diffraction peaks, which

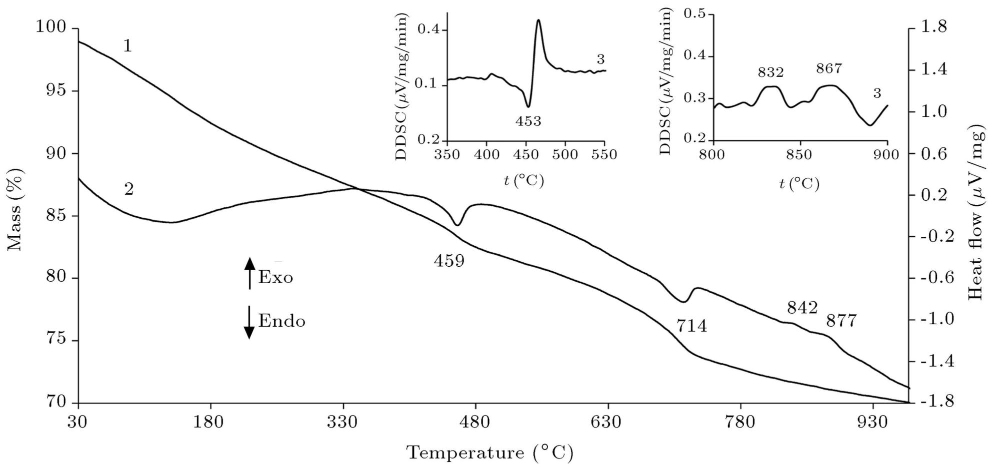


**Figure 2.** TGA (curve 1), DSC (curve 2), and DDSC (curve 3) curves of the synthesized product, when the duration of hydrothermal treatment at 200°C temperature is 4 h.

**Table 2.** Dependence of pH value of medium and the heat of thermal effects typical for $\alpha$-$C_2SH$, C-S-H(I) and C-S-H(II) on duration of synthesis.

| **Hydrothermal synthesis duration, h, at 200°C temperature*** | **pH value of medium** | **Heat of thermal effect (J/g)** | | |
|---|---|---|---|---|
| | | **Temperature range (°C)** | | |
| | | **400-500** | **830-850** | **850-880** |
| | | **$\alpha$-$C_2SH$** | **C-S-H(I)** | **C-S-H(II)** |
| 4 | 12.39 | — | 1.53 | 5.61 |
| 8 | 12.37 | 58.55 | 0.11 | 7.32 |
| 16 | 12.25 | 94.03 | 0.8 | 6.72 |
| 24 | 12.15 | 16.97 | 6.39 | — |
| 72 | 11.90 | — | 3.59 | — |

*: 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 $\alpha$-$C_2SH$ and $CaCO_3$ in the synthesis products.

| **Hydrothermal synthesis duration, h, at 200°C temperature*** | **Data according to the TGA method** | | | |
|---|---|---|---|---|
| | **Mass losses at 400-500°C (%)** | **Quantity (%)** | **Mass losses at 650-750°C (%)** | **Quantity (%)** |
| | **$\alpha$-$C_2SH$** | | **$CaCO_3$** | |
| 4 | — | — | 3.23 | 7.34 |
| 8 | 4.45 | 48.95 | 3.01 | 6.84 |
| 16 | 4.37 | 48.07 | 3.73 | 8.48 |
| 24 | 1.96 | 21.56 | 1.27 | 2.89 |
| 72 | — | — | 2.01 | 4.57 |

*: 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.

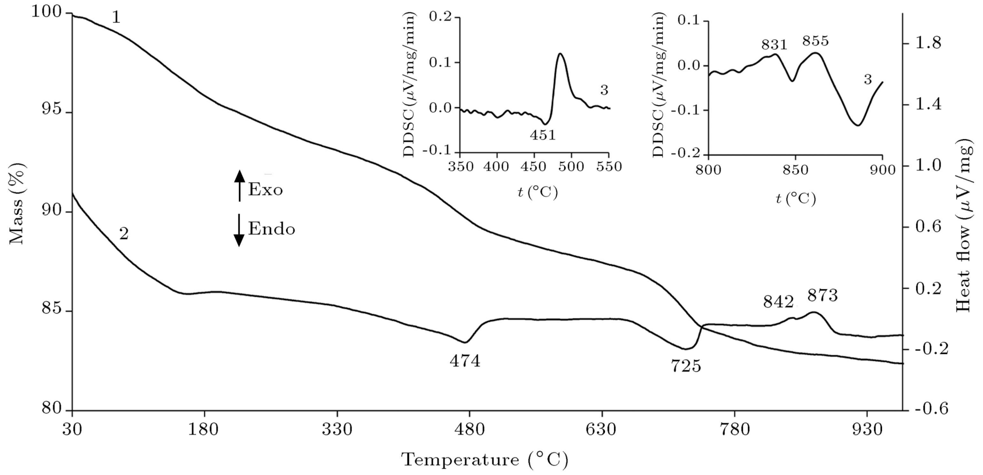


**Figure 3.** TGA (curve 1), DSC (curve 2), and DDSC (curve 3) curves of the synthesized product, when the duration of hydrothermal treatment at 200°C temperature is 8 h.

*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 $\alpha$-$C_2SH$ recrystallization (Figure 1, curve 3). DSC data confirmed that a larger amount of the main synthesized product, $\alpha$-$C_2SH$, 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 $\alpha$-$C_2SH$ was formed (Table 3).

Unexpected results were obtained after 24 h of hydrothermal treatment; a recrystallization of $\alpha$-$C_2SH$ to kilchoanite (*d-spacing*-0.355; 0.304; 0.288; 0.267),

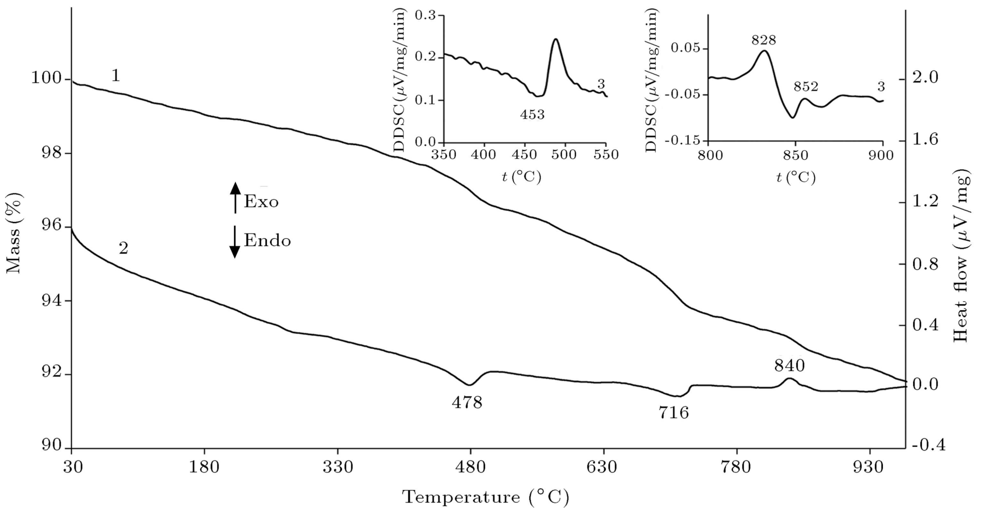


**Figure 4.** TGA (curve 1), DSC (curve 2), and DDSC (curve 3) curves of the synthesized product, when the duration of hydrothermal treatment at 200°C temperature is 24 h.

which is not consisted of water ($Ca_6(SiO_4)(Si_3O_{10})$), 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 $\alpha$-$C_2SH$ 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 kilchoanite resistance to carbonization. Moreover, an exothermic effect typical for C-S-H(II) 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 $\alpha$-$C_2SH$ at 200°C, kilchoanite was also formed in the products. In this case, $\alpha$-$C_2SH$ was prepared from $\beta$-$C_2S$ 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 kilchoanite 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 $H_2O$ vibrations was observed. The assumption that the structure of kilchoanite does not contain any water was proven by the low intensity absorption maximums at ~ 1620 and ~ 3482 $cm^{-1}$. In bending $\delta$(Si-O-Si) and $\delta$(O-Si-O) vibrations range, two absorption bands at ~ 434, ~ 583 $cm^{-1}$ and the doublet at ~ 495, ~ 516 $cm^{-1}$ were identified. Meanwhile, a triplet at ~ 896, ~ 930, ~ 977 $cm^{-1}$, which can be attributed to symmetrical $\nu_s$(O-SiO-) stretching signals, was observed. Two absorption bands assigned to asymmetrical $\nu_{as}$ (Si-O-Si) stretching vibrations were identified at ~ 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 ~ 710 $cm^{-1}$ was also observed, reflecting the symmetrical $\nu_s$(Si-O-Si) stretching vibrations. Moreover, the absorption maximum at ~ 1282 $cm^{-1}$ can be assigned to bending $\delta$(OH(Si)) signals.

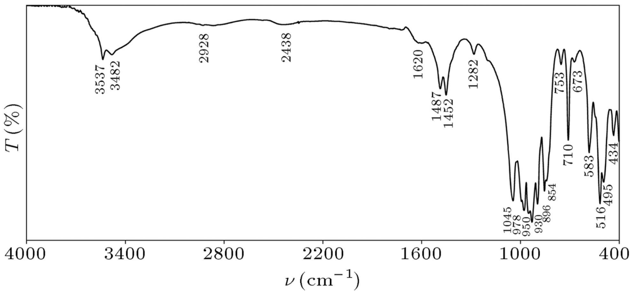


**Figure 5.** FT-IR spectrum of synthesis products, when the duration of hydrothermal treatment at 200°C temperature is 24 h.

Furthermore, after extending the duration of isothermal curing to 48 and 72 h, $\alpha$-$C_2SH$ was fully recrystallized to kilchoanite due to undetected diffraction maximums specific to $\alpha$-$C_2SH$ in XRD patterns (Figure 1, curve 4). Also, an endothermic effect at ~ 460°C temperature, which can be assigned to the latter compound, is not visible (Figure 6). Furthermore, thermal conversions attributed to kilchoanite as well as the removal of crystallization water are not observed in DSC curves. ~ 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

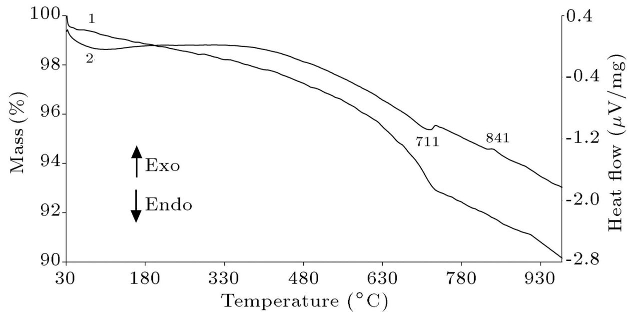


**Figure 6.** TGA (curve 1) and DSC (curve 2) curves of synthesis product, when the duration of hydrothermal treatment at 200°C temperature is 72 h.

changes appeared in FT-IR spectrum; only absorption band, reflecting bending $\delta(H_2O)$ 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:

$$1{,}5\mathrm{CaO}+\mathrm{SiO_2}.n\mathrm{H_2O}+10\mathrm{H_2O}\xrightarrow{4\text{ h}}\left|\begin{array}{l}\alpha\text{-C}_2\text{SH}\\ \text{C-S-H(I)}\\ \text{C-S-H(II)}\\ \text{CaCO}_3\\ \text{Ca(OH)}_2\end{array}\right.$$

$$\xrightarrow{8\text{ h}}\left|\begin{array}{l}\alpha\text{-C}_2\text{SH}\\ \text{C-S-H(I)}\\ \text{C-S-H(II)}\\ \text{CaCO}_3\end{array}\right.\xrightarrow{24\text{ h}}\left|\begin{array}{l}\text{C-S-H(I)}\\ \alpha\text{-C}_2\text{SH}\\ \text{kilchoanite}\\ \text{CaCO}_3\end{array}\right.$$

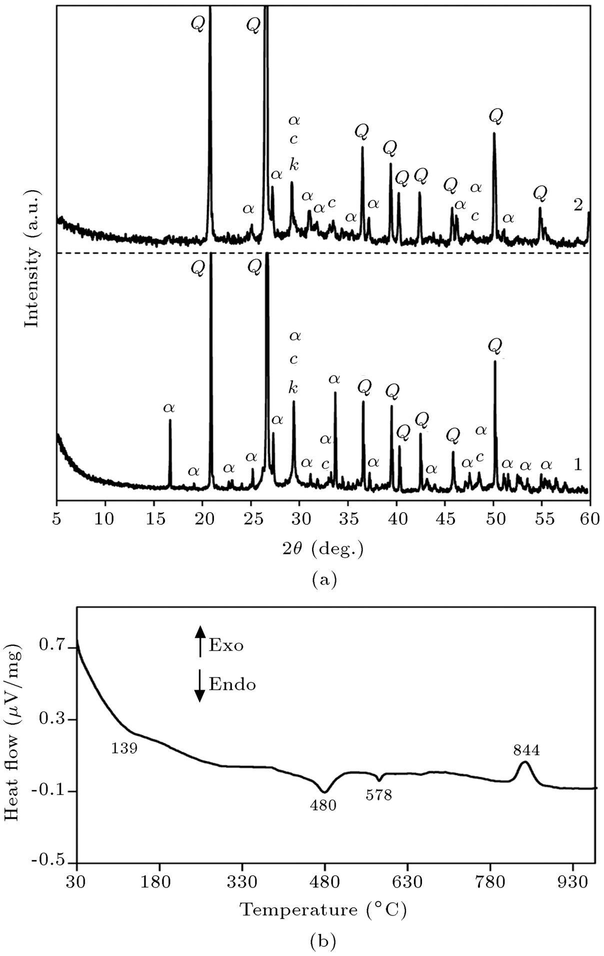
$$\xrightarrow{48\text{-}72\text{ h}}\left|\begin{array}{l}\text{kilchoanite}\\ \text{C-S-H(I)}\\ \text{CaCO}_3\end{array}\right. \qquad (1)$$

Thus, $\alpha$-$C_2S$ hydrate can be synthesized from a non-stoichiometric composition (the molar ratio $C/S = 1.5$) of CaO and $SiO_2.nH_2O$ in unstirred suspensions. $\alpha$-$C_2SH$ 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 $\alpha$-$C_2SH$ was used to prepare some hydraulic cementitious 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 $\alpha$-$C_2SH$, 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 disordered state on the silicate surfaces [15].

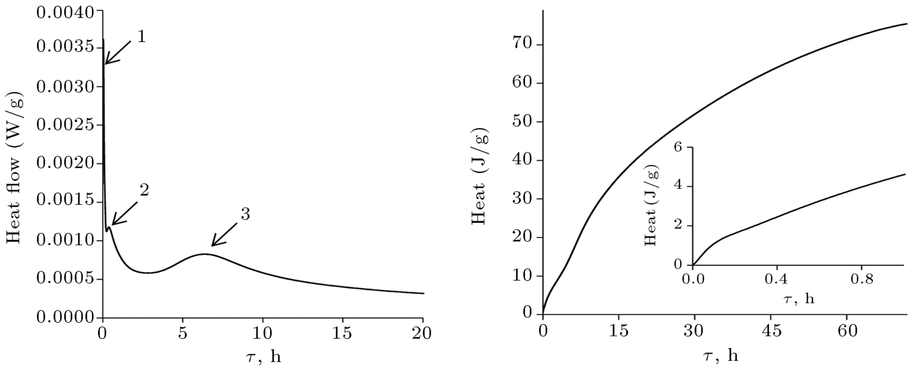
For these reasons, the Binder Material (BM) was prepared by mixing $\alpha$-$C_2SH$ ($C/S = 1.5$; 16 h, 200°C) and quartz sand (1:1 by mass) in a homogeniser (Turbula) at 34 rpm for 30 min. Later on, BM sample was ground in a vibrating cup mill ("Pulverisette 9") at 950 rpm for 4 min. It was determined that after grinding, the BM sample was significantly amorphized. This fact was confirmed by XRD analysis: the intensity of diffraction peaks specific to $\alpha$-$C_2SH$ (*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



(a)

(b)

**Figure 7.** (a) XRD (curve 1: after mixing; curve 2: after ground). (b) DSC after ground. Indexes: c–C-S-H; $\alpha$–$\alpha$-$C_2SH$; $Q$–quartz.



(a) (b)

**Figure 8.** Heat evolution rate (a) and cumulative heat (b) of BM sample.

known [30] that the amount of the decomposed $\alpha$-$C_2SH$ 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 $\alpha$-$C_2SH$, BM samples were burned at 450°C for 30 min under air atmosphere. As it was expected, after calcination, the complete destruction of $\alpha$-$C_2SH$ 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 hydraulic reactions between BM and water after wetting process (2 and 3 exothermic reactions) can be described by this hypothetical reaction:

$$\mathrm{C_{1.5}S_1+}x\mathrm{Q+H_2O\rightarrow C_{1.5}S_{(1+}}y\mathrm{_)H+(}x-y\mathrm{)Q+\Delta H}, \qquad (2)$$

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; ΔH 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 $50 \pm 5$°C, and put through a sieve with an 80-$\mu$m 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 $\alpha$-$C_2SH$ (*d-spacing*: 0.326; 0.266; 0.241 nm) were identified (Figure 11(a)).

XRD results were confirmed by DSC data. The

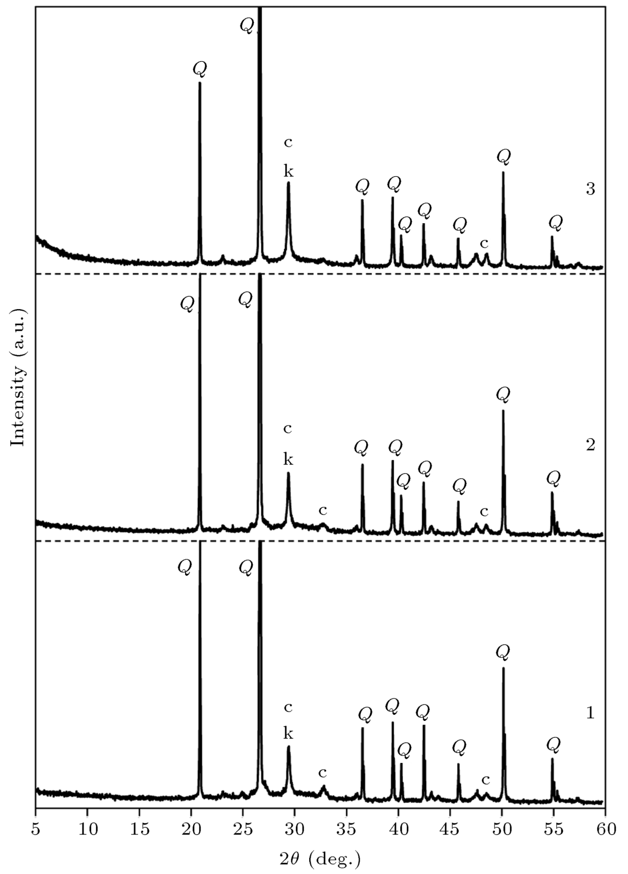


**Figure 9.** XRD patterns of BM sample when durations of hydration are, 1-0 h; 2-1.8 h; 3-12 h. Indexes: *Q*–quartz; c–C-S-H; k–$CaCO_3$.

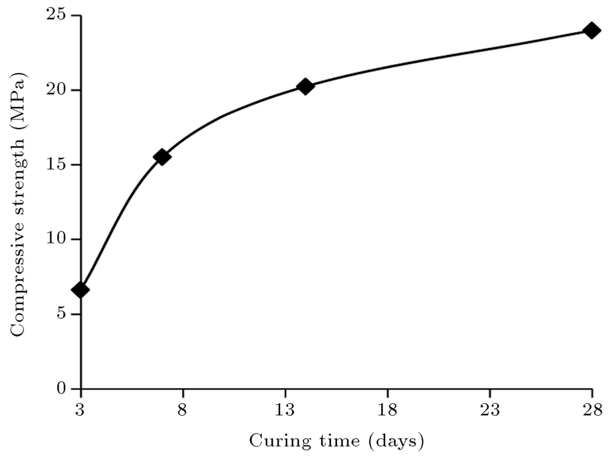


**Figure 10.** Compressive strength of BM samples.

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 $\alpha$-$\beta$ 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 $\alpha$-$C_2SH$ basis. The results presented here show that the $\alpha$-$C_2SH$, 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 $\alpha$-$C_2SH$ as alternative cementitious material, the setting and hardening characteristics will be performed by making mortar and concrete.

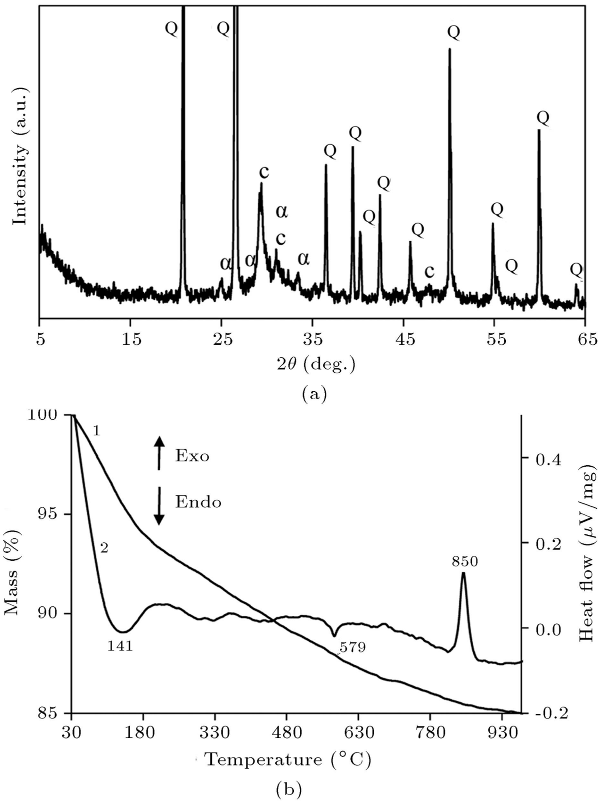


**Figure 11.** XRD (a) and STA (curve 1: TGA; curve 2: DSC) (b) of BM sample cured at 20°C for 28 days. Indexes: c–C-S-H; $\alpha$–$\alpha$-$C_2SH$; *Q*–quartz.

## 4. Conclusions

1. When the molar ratio $CaO/SiO_2$ of primary mixture was equal to 1.5, it was determined that in unstirred $CaO–SiO_2.nH_2O–H_2O$ suspensions, within 4 hours of isothermal curing at 200°C, dicalcium silicate hydrates –$\alpha$-$C_2SH$, 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 $\alpha$-$C_2SH$ is a domination mineral in the synthesis product after 16 h of curing.
2. At 200°C, after 24 h of hydrothermal treatment, $\alpha$-$C_2SH$ starts to recrystallize into kilchoanite. Furthermore, after extending the duration of isothermal curing to 48 h, $\alpha$-$C_2SH$ 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-$C_2SH$-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.

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