

Preparation of a Novel Cementitious Material from Hydrothermally Synthesized C–S–H Phases

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New cementitious materials based on calcium hydrosilicate hydrates were recently developed as potential substitutes for ordinary portland cement, but with a reduced CO₂ footprint. The materials are produced by hydrothermal processing of SiO₂ and Ca(OH)₂, giving rise to calcium silicate hydrates, followed by mechanical activation of the latter via cogrinding with various siliceous materials. Thus, the chemical composition in terms of C/S ratio could be adjusted over a broad range (1-3). In this study the synthesis of a previously unknown cementitious material produced via the combination of mechanical activation in a laboratory mill and thermal treatment of a mixture of quartz and hydrothermally synthesized calcium silicate hydrates: α -Ca₂[HSiO₄](OH) (α -C₂SH) and Ca₆[Si₂O₇] (OH)₆ (jaffeite) are reported. It forms independently of the type of mill used (eccentric vibrating mill, vibration grinding mill) after thermal treatment of the ground materials at 360°C-420°C. The new material is X-ray amorphous and possesses a CaO/SiO₂ ratio of 2. A characteristic feature in regards to the silicate anionic structure is the increased silicate polymerization (up to 27% Si₂O₇ dimers) as revealed by the trimethylsilylation method. Infrared (IR) spectra show a very broad absorption band centered at about 935 cm⁻¹. Another characteristic feature is the presence of ~2.5 wt% H₂O as shown by thermogravimetry (TG) coupled with IR spectroscopy. As this water is bound mostly as hydroxyl to Ca, we refer to this new cementitious material as calcium-oxidehydroxide-silicate (C-CH-S). Calorimetric measurements point to a very high hydraulic reactivity which is beyond that for typical C₂S materials. The influence of the type of grinding on the thermal behavior of α -C₂SH upon its transformation into water-free Ca2SiO4 modifications is discussed.

I. Introduction

E FFORTS to reduce the CO₂ emissions from the production of ordinary portland cement have resulted in several approaches which have been proposed recently. Reduction in the CaO/SiO₂ (C/S) ratio of the starting materials and burning at lower temperature (about 1300°C) is one of the most common approaches which has been pursued by the production of the so-called belite or belite sulfoaluminate cements for many years. Stabilization of C₂S modifications β -C₂S and α'_L -C₂S with different dopants is one key issue in this case. Excellent reviews of this topic have been written by both Chatterjee^{1,2} and Gartner.³

A completely different approach uses a hydrothermal process for the synthesis of precursors with a targeted C/S ratio of almost 2 which in a subsequent step can be directly used for production, via thermal treatment, of C₂S modifications. In this case, temperatures much lower than 1300°C are sufficient. Several variations in this approach are described in literature, differing mostly in the starting materials, e.g., fly ash⁴⁻⁷ recycled concrete,^{8,9} or reagent-grade chemicals, such as quartz, amorphous silica, and Ca(OH)₂ or CaO.¹⁰ Nevertheless, all these approaches are similar in two aspects: (1) all of them aim at the synthesis of α -Ca₂[HSiO₄](OH) (α -C₂SH) as a crystalline calcium silicate hydrate precursor (with a few exceptions on a laboratory scale where hillebrandite, $Ca_2[SiO_3](OH)_2$, was synthesized);¹¹⁻¹⁴ and (2) the cementitious material resulting from the subsequent thermal treat-(500°C-1000°C) is always a crystalline C₂S ment polymorphic modification: β -C₂S, x-C₂S, or α'_1 -C₂S. As the thermal behavior of the precursor (in this case α -C₂SH) is central to potential industrial applications, significant effort has been expended in its characterization. However, the results of different authors vary greatly regarding the temperature of dehydration of α -C₂SH, and furthermore there is an even greater discrepancy concerning the resulting polymorphs of $C_2S^{10,15,16}$ and possible hydrated intermediate phases.¹⁷

Recently, another two-step approach, called "Celitement", has been proposed which is based on the hydrothermal preparation and further mechanochemical treatment of calcium silicate hydrates (amorphous C–S–H or crystalline precursor α -C₂SH, jaffeite, Ca₆[Si₂O₇](OH)₆, etc., with C/S of between 1 and 3) together with a siliceous substrate (quartz sand, granulated blast furnace slag, glass, etc.),¹⁸ to yield a final C/S ratio < 1. Additional information about potential CO₂ and energy savings and Celitement types is given in Ref. [19–23]. For additional information about Celitement and the operation of the pilot plant (Celitement GmbH, Eggenstein-Leopoldshafen, Germany). The final cementitious Celitement is an amorphous calcium hydrosilicate hydrate (CHSH) which contains about 6%–8% H₂O bound in Ca–OH, Si–OH, and H₂O environments.

In this manuscript, we describe a modification in the Celitement process that includes three preparation steps: (1) hydrothermal synthesis; (2) mechanochemical treatment; and (3) subsequent thermal treatment at low temperature (300° C– 500° C). In this manner, the resulting cementitious material possesses the same C/S ratio, but has a reduced water content of 1%–1.5% compared to CHSH. This manuscript also presents some important structural properties of the resulting new cementitious material that has been identified as an amorphous calcium silicate hydroxide with water bound preferentially in Ca–OH environments, and subsequently referred to as (C–CH–S).

II. Experimental Procedure

(1) Sample Preparation

Two different series of samples, called Exzenter Schwingmühle (ESM) and Scheiben Schwingmühle (SSM), were produced according to three-step procedures as described below.

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(A) ESM Series: (1) First, a precursor was hydrothermally synthesized. As starting materials Ca(OH)₂ p.a., SiO₂ (Quartz, Merck p.a.), 1M NaOH, and H₂O were used. The materials were mixed in a C/S of 2 and a water/solid ratio also of 2. The resulting mixture was treated hydrothermally at 190°C and saturated steam pressure for 6 h in a specially designed autoclaving system developed by PREMEX REAC-TOR AG (Lengnau, Switzerland) with permanent stirring. The volume of the autoclave is 31 and allows the production of 700-1000 g hydrothermal product. The resulting product was dried for 24 h at 70°C in a drying oven. (2) In the second step, 1000 g hydrothermal product was ground together with 1000 g quartz sand (96 wt% quartz) in an eccentric vibrating mill, ESM (SIEBTECHNIK, Mühlheim/Ruhr, Germany) for 4 h. The sample produced in this way was labeled ESMRT. This synthesis corresponds to the "Celitement" process and contains CHSH as the cementitious component. (3) Finally, the ground product was heated at 300°C, 320°C, 340°C, 360°C, 380°C, 400°C, 420°C, 440°C, 460°C, and 500°C for 6 h in air. The final products of this series are referred to as ESM300, ESM320, etc. In addition, three analogous grindings were prepared to prove the reproducibility of the results. These were labeled ESM56 (with subsequent thermal treatments at 200°C, 400°C, and 460°C), ESM65 (treatments at 200°C, 400°C, and 460°C), and ESM91 (treatments at 300°C, 400°C, and 460°C), and are considered only in chapter Trimethylsilylation.

(B) SSM Series: Synthesis of the SSM series comprised similar steps, including a hydrothermal process as described above, followed by grinding with quartz sand (50%/50% by weight resulting in a total of 100 g mixture) as described above, the difference being that grinding was using a vibration grinding mill, SSM (HERZOG Maschinenfabrik GmbH & Co. KG, Osnabrück, Germany) for 12 min. The sample corresponding to this product is referred to as SSMRT, again containing CHSH as cementitious phase. In a third step, the ground material was heated at 370°C, 420°C, 440°C, and 460°C for 6 h. The final products were labeled SSM370, SSM420, SSM440, and SSM460 once again with reference to the temperature of treatment.

All samples were investigated by XRD, thermal analysis (TA), IR spectroscopy, Trimethylsilylation (TMS), gas adsorption after the method developed by Brunauer-Emmett-Teller (BET), and Calorimetry. Because of the limited scaleup possibility of the vibration grinding mills we present only limited analytical results for the SSM series.

(2) XRD

The samples were investigated by X-ray diffraction using MPD Xpert-pro (PANalytical, Almelo, Netherlands) equipped with a multistrip PIXell detector (255chanels, $3.347^{\circ}2\Theta$) and Cu-radiation. The Cu K_{β} was filtered with Ni-filter. The measurements were taken with soller slits 0.04 rad (2.3°) and adjustable slits giving a constant irradiated sample length of 10 mm. For the purpose of phase identification, the software packages Highscore-Plus (PANalytical) and Diffrac-Plus (Bruker-AXS, Karlsruhe, Germany) were used. Quantitative phase analyses by the Rietveld method were performed with TOPAS V4.2 (Bruker-AXS, Karlsruhe, Germany).

(3) Thermal Analysis

Simultaneous thermogravimetric and differential thermal analysis measurements (TG/DTA) were performed using a SEIKO TA-Disc-Station with TG/DTA 320 module (Seiko Instruments Inc., Chiba, Japan). Measurements were performed in Pt/Rh crucibles over the range 30° C-1000°C with 10°C/min heating rate under nitrogen flux. To differentiate between H₂O and CO₂ release, eight samples (untreated mixture, ESMRT, ESM300, ESM340, ESM380, ESM420, ESM460, and ESM500) were measured additionally with a

Jupiter 449-F3 balance from NETZSCH coupled with a FTIR-cell, optical path length of 123 mm, and sandwich KBr and ZnSe-windows for simultaneous measurements of the gas phase with infrared spectroscopy. The IR measurements were taken with a TENSOR 27 spectrometer (Bruker Optics, Ettlingen, Germany) with MCT detector with spectral resolution 4 cm⁻¹. Recording frequency of spectra was every 15 s. The transfer line from the TA unit and the FTIR cell was heated to 200°C to avoid condensation and constantly purged with N₂ with gas flow of 70 mL/min. Quantitative determinations of H₂O and CO₂ were performed using the method described in Ref. [24].

(4) Trimethylsilylation

Silicate speciation was determined by trimethylsilylation and subsequent gas chromatography with flame-ionization detection (GC-FID) based on a procedure by Hoebbel et al.²⁵ Solids (approx. 10 mg) were dissolved and silylated for 15 min in a continuously stirred mixture of 10 mL dimethylformamide, 8 mL hexane, and 2 mL TMS at room temperature. Stirring was continued for another 15 min at room temperature and afterward, 40 mL H₂O was added. The solution was prepared by phase separation (organic/inorganic) and washing of the organic phase three times with 420 mL of water prior to being injected into the GC-FID system. The method allows to measure relative proportions of small silicate species from monomers up to pentamers with a relative error of $\pm 10\%$. Results are not directly transferable to absolute contents, as the yields vary for different samples. In our experience with reference substances, yields between 70% and 80% of the measurable species are typical, with the lower values correlating with higher proportions of silanol.

(5) GC-FID

A gas chromatograph Agilent 5890, equipped with a 30 m capillary column DB1HT, was used for the analysis. The GC analysis was carried out in constant pressure mode (25 psi) using an oven temperature programmed to rise from 80° C (held for 1 min) to 340°C (held for 10 min) at 12°C/min. Retention times (minutes) were as follows: (TMS)₄SiO₄: 4.23, (TMS)₆Si₂O₇: 9.45, (TMS)₈Si₃O₁₀: 14.08, (TMS)₁₀Si₄O₁₃: 18.02, (TMS)₁₂Si₅O₁₆: 21.38.

(6) Infrared Spectroscopy

Infrared spectroscopy measurements were performed on KBr pellets produced from mixtures of 200 mg KBr and 0.5 mg sample. The pellets were measured on an IFS66v spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a GLO-BAR source and MCT detector. Spectra were taken in the range $600-4000 \text{ cm}^{-1}$ with a spectral resolution of 4 cm⁻¹.

(7) **BET**

Powder samples of 200–500 mg were dried at 105°C and 1 mbar vacuum for 16–18 h, usually overnight. Specific surface area (SSA) was measured at six different points of relative pressure $p/p_0:0.05-0.1-0.15-0.2-0.25-0.3$ using a Quantachrome Nova 4000e (Quantachrome Instruments, Boynton Beach, FL) with Nitrogen as probe and liquid nitrogen as coolant. Subsequently, fitting was performed according to the BET theory.²⁶ Experiments with absolute surface areas lower than 1 m² were repeated with larger sample masses.

(8) Calorimetry

Calorimetric investigations were performed with a TAM Air 8 channel calorimeter (TA instruments, New Castle, DE). After equilibration of the samples (1 g each) in a 20 mL glass Admix ampoule at 20°C for 12 h, water was added in a



Fig. 1. Comparison of the phase compositions (determined by quantitative XRD with the Rietveld method) of the hydrothermal product (HP), mixture HP+quartz, and the ground mixtures ESMRT and SSMRT (left) and their corresponding IR spectra (right).

w/s ratio of 1. Measurements of the heat release as result of hydration of the samples were performed within 70–150 h periods.

III. Results and Discussion

(1) XRD

After hydrothermal treatment, the product (HP) consisted of α -C₂SH as the main constituent (67 wt%), with 7 wt% Ca₆[Si₂O₇](OH)₆ (jaffeite), 3.8 wt% quartz, and negligible quantities of portlandite and CaCO₃ (calcite). XRD showed about 19 wt% amorphous content. Figure 1 (left) shows the phase composition of the hydrothermal product (HP), mixture with quartz, and the ground samples at room temperature with ESM and SSM mill correspondingly.

(2) Series ESM

The XRD pattern of the ground product (ESMRT, Fig. 2) was dominated by reflections due to quartz. In addition, reflections typical for α -C₂SH (ICDD entry Nr. 82-1211) were present. Quantitative analysis showed a substantial increase in the amorphous content of the ground sample (35.6 wt%) compared to the mixture HP-quartz (11.3 wt%). At the same time the secondary phases like calcite, portlandite, and jaffeite were not detected by XRD and the content of α -C₂SH was substantially decreased. As a result of the grinding, the detectable quantity of quartz decreased by 5%. The XRD patterns of the materials heated at temperatures between 300°C and 340°C showed a significant decrease in the intensity of α -C₂SH with increasing temperature (Fig. 2). In samples treated at temperatures between 360°C and 420°C, only reflections of quartz were present. It was not until temperatures above 440°C that reflections of C₂S polymorphic modifications, x-C₂S and γ -C₂S, became visible in the XRD patterns. With further increases in temperature, increasing amounts of these crystalline C₂S modifications were observed (Figs. 2 and 3).

(3) Series SSM

The qualitative phase composition of the product after grinding (labeled SSMRT) was similar to that of ESMRT comprising quartz and minor amounts of α -C₂SH (Fig. 1). The quantitative analysis pointed to a higher degree of grindinginduced amorphization than that for the ESMRT sample,



Fig. 2. XRD patterns of the hydrothermal product ground with quartz sand (RT) in an eccentric swing mill (ESM series) and of the samples thermally treated in the range 300°C–500°C. The patterns between the arrows correspond to the formation of the amorphous cementitious material C–CH–S (360°C–420°C). At higher temperatures, a formation of x-C₂S and γ -C₂S takes place.

leading to almost 45 wt% amorphous component. Correspondingly, the quantity of α -C₂SH decreased to 11 wt%. The amorphization of quartz was of a similar order (6%) to





Fig. 3. XRD patterns of the hydrothermal product ground with quartz sand (RT) in a vibration grinding mill (SSM series) and of the samples thermally treated in the range $370^{\circ}\text{C}-460^{\circ}\text{C}$. The patterns between the arrows correspond to the formation of the amorphous cementitious material C–CH–S ($360^{\circ}\text{C}-420^{\circ}\text{C}$). At higher temperatures a formation of α'_{L} -C₂S takes place.

the ESMRT sample. Comparing the IR spectra of SSMRT, ESMRT, and HP confirmed the XRD results, with a decrease after grinding in the intensity of the α -C₂SH and jaffeite bands (Fig. 1, right). The assignment of the observed IR bands is given in Table I. In XRD patterns of the products treated at 370°C and 420°C (SSM370, SSM420, respectively), quartz was the only crystalline phase present, whereas samples treated at 440°C and 460°C also showed evidence of α'_L -Ca₂SiO₄ (α'_L -C₂S), (squares in Fig. 3).

Therefore, in both series, an amorphous phase appeared to form, which mostly originated from the main components of the hydrothermal product α -C₂SH and jaffeite. This phase has already been described as an amorphous CHSH of Celitement type,^{18–22} which is characterized by the presence of about 5% H₂O as both OH groups and molecular H₂O. The molecular H₂O is formed by partial hydrolysis and condensation of OH groups. The OH groups are bound to both Ca and Si. Partial polymerization of monomeric SiO₄ tetrahedra to dimeric Si₂O₇ and even higher polymeric silicate species also takes place as a result of grinding.

Obviously, another amorphous phase (with considerably reduced H₂O content) was formed in the temperature range $370^{\circ}\text{C}-420^{\circ}\text{C}$ due to the reaction and dehydration of α -C₂SH and the amorphous CHSH of the Celitement type which was present at RT. This amorphous product transforms into C₂S at temperatures above 420°C. There is an obvious discrepancy regarding the temperature of dehydration of α -C₂SH between the results from the TA and ex situ thermal treatments, i.e., 460°C-470°C, Fig. 4 and 370°C-420°C, respectively. This deviation is due to different experimental conditions between the sample treatment and the TA experiment (prolonged treatment at constant temperature and heating rate of 10°C/min) resulting in differences in the reaction kinetics. Considering these results two interesting phenomena were observed. First, after thermal treatment at temperatures higher than 420°C ESM and SSM, both contained Ca₂SiO₄ (C_2S) in addition to quartz, but the C_2S polymorphic modifications were different. In the case of the ESM series, there was formation of γ -C₂S and x-C₂S, whereas in the SSM series a'L-C2S was formed. This suggests the formation of different nanoscale structures in the two different mills, ESMRT and SSMRT. There are various studies of the thermal behavior of α -C₂SH that point to a rather complicated and unpredictable dehydration mechanism. Different authors show formation of γ -C₂S,^{27,28} x-C₂S,¹⁰ β -C₂S,^{29,30} or dellaite.¹⁷ As a possible explanation of such variability, a diversity of the starting materials or crystal size effects is often considered. Second, there was formation of α'_1 -C₂S at temperatures as low as 440°C, although this polymorphic modification is normally known to be stable at higher temperatures (675°C–1177°C).^{31–33} Together with β -C₂S and C₄A₃S (yeelimite), α'_L -C₂S is one of the most abundant phases in belite sulfoaluminate cements that are burned at temperatures some 200°C lower than portland cement.^{34,35} Alpha'_L-C₂S is normally stabilized by the presence of impurities, e.g., MgO,

Table	I.	IR	Bands	Assignment
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Band assignment	$\alpha - C_2 SH$	Jaffeite	Quartz	СН	CHSH	C–CH–S	$x-C_2S$
Libration OH (Ca)	671 709	694					
v ₁ Si–OH	754				746 761		
v ₁ Si–O	861	830	778 798				
v ₃ Si–O	944 981 995 s.				960 vb.	935 vb.	850 s [†] 875 s [†] 950 [†]
v ₃ Si–O–Si (Q ¹) v ₃ Si–O–Si (Q ⁴)		1054	1096 1172				990
δ-OH—O δ-H–O–H (H ₂ O)	1281				1610	1610	
v_1 OH(Si)–B v_1 OH(Si)–A	2450 2850						
v ₁ OH(Ca)	3537	3607 3624		3643	3560 vb. asymm.	3540 vb. asymm.	

[†]Interference with bands of γ -C₂S.

Asymm., asymmetrical shape; Q¹–Q⁴, number of bridging oxygen atoms in the silicate structure; S, shoulder; vb, very broad.



Fig. 4. Weight-loss curves of the samples of the ESM series (top) and SSM series (bottom). Samples ESM380, ESM400, ESM420, SSM370, and SSM420 show very similar curves corresponding to C–CH–S.

K₂O, BaO, and SO₃³⁶ or Na₂B₄O₇·10H₂O (borax).³⁷ Kacimi et al. reported the synthesis of α'_L -C₂S from fly ash with hydrothermal pretreatment at temperatures as low as $800^{\circ}C$.³⁸ Formation of a poorly crystalline β -C₂S was reported after grinding of pure α -C₂SH in an SSM mill at RT.³⁹ The authors described the formation of well-crystalline β -C₂S after thermal treatment of the ground material at 400°C and of α'_{L} -C₂S at 500°C. Thus, in the products of the SSM series presented here, β -C₂S-like domains are probably present, which may act as nucleation centers undergoing a transformation into a'_L-C₂S upon heating above 440°C. One possible mechanism for stabilization of β-C₂S upon grinding might be the presence of OH defects in its structure as pointed out by Roy³¹ [and references therein], who also discussed the inverse dependence of the phase transition temperature of β -C₂S upon crystal size and strain. Ishida et al.¹⁴ also described lowering of the transition temperature of β -C₂S as a result of grinding.

(4) Thermal Analysis

The TG curves (from RT to 1000°C) of both sample series are plotted in Fig. 4, whereas Fig. 5 gives quantitative information about H₂O and CO₂ release. The TG curves could be subdivided into three temperature ranges, comprising RT– 350° C, 350° C– 750° C, and 750° C– 1000° C (Fig. 6). The weight loss of the starting mixture HP + Quartz observed upon heating to 1000°C (Fig. 4) was primarily due to the dehydration of α -C₂SH (specific water content 9.45%) and jaffeite (11.78%) between 350°C and 750°C (4.82%). The virtual absence of portlandite (see XRD) meant that its contribution



Fig. 5. IR absorption of CO_2 (top) and H_2O (bottom) released in the gaseous phase of the samples of the ESM series during thermal analysis as function of temperature measured with TG-FTIR (top).

to this loss was negligible. The amorphous phase shown by XRD to be present (18.3%) had a water content of about 10% and did not contain measurable quantities of C–S–H, which would dehydrate well below 300°C. Rather, it was assumed to comprise a mixture of nanocrystalline α -C₂SH and jaffeite. The total weight loss of 5.37% was consistent with the phase composition observed by XRD considering that a small part of the weight loss was due to calcination of crystalline CaCO₃ (calcite), evidenced by the sharp peak above 600°C in the plot of the CO₂ absorption versus temperature (Fig. 5, top). The calcite content was calculated to be 1.3–1.4 wt%.

(5) Series ESM

Grinding of the starting mixture HP + Quartz had a great influence on the thermal properties of the product. The most striking difference between the TG curves of the starting mixture and the ground sample was seen in the shift of the weight loss from 350° C- 750° C to lower temperatures due to grinding (Fig. 6). Thus, the weight loss between RT and 350° C increased from 0.3 to 1.9 wt%, whereas that between 350° C and 750° C decreased from 4.82 to 2.9 wt% in the ground sample (Fig. 6, top). The change is clearly seen in Fig. 5 (bottom) which represents the H₂O absorption measured with IR as a function of temperature. Therefore, a partial transformation of the crystalline calcium silicate hydrates occurred upon grinding. This behavior has already been observed and described elsewhere^{8,9,18-20} and is typical in the



Fig. 6. Weight loss of the samples from ESM (top) and SSM series (bottom) over different temperature ranges: total weight loss (RT–1000°C, down pointing triangles) RT–350°C (squares), 350°C-750°C (circles), and 750°C-1000°C (up pointing triangles). The CO₂ loss (stars) and H₂O loss (diamonds) given in the graph for the ESM series (top) are determined quantitatively by IR spectroscopy. The samples treated at 380°C-420°C (highlighted with rectangles in both graphs) show almost constant weight loss over the range 350°C-750°C pointing to a relative stability of the phases after treatment at 380°C-420°C. Note the increased weight loss over the range RT–350°C (circles) after grinding, which is higher for the treatment with the vibration grinding mill (SSM).

formation of cementitious amorphous CHSH of the Celitement type. Grinding also had a great influence on calcite which was no longer detectable. The decarbonation of the ground (and heated) samples can be subdivided into three events: small uniform CO2 release between 400°C and 700°C (seen as two broad "humps" in Fig. 5, top) and a sharp event at about 840°C. The step at 840°C in the TG curves of all ground samples in Fig. 5 is therefore definitely due to decarbonation. In addition, there was no dehydroxilation at temperatures above 650°C (Fig. 5, bottom). Thermal treatment led to clear differences in the thermal behavior of the ground sample. Whereas the nonthermally treated sample (RT) showed a weight loss of about 5 wt%, primarily due to dehydration at temperatures below 350°C, the samples treated at 360°C-420°C only lost 1.2-1.5 wt% and those treated at 500°C just 0.5 wt%. There was a striking similarity in the TG curves of the samples heated to 380°C-420°C. Quantitative determinations by IR spectroscopy revealed 0.9-0.8 wt% H₂O content in these samples. The total weight loss over the range 25° C-1000°C of these samples was mostly between 350° C and 750° C (Fig. 6, top), implying a loss mostly of hydroxyl groups. In addition, the decomposition of amorphous CaCO₃ would have slightly contributed to that weight loss. The "plateau" seen over the range 350° C- 750° C (Fig. 6) points to the stability of a new amorphous calcium silicate hydroxide phase with reduced water content. This water was present in the form of OH groups in Ca–OH linkages (see *IR*) CaO–Ca(OH)₂–SiO₂, [C–CH–S].

The CO₂ loss determined by IR spectroscopy varied between 0.6 wt% (hydrothermal product) and 0.4 wt%. Thus, considering Fig. 5, it appears that the weight loss between 750°C and 1000°C (varying between 0.16 and 0.35 wt%) was caused by the complete decarbonation of the amorphous CaCO₃ tightly bound in the calcium silicate matrix upon grinding. Although the TG curves of the ground samples SSMRT and ESMRT were visibly different (due to the different degree of amorphization of HP), the TG curves of the samples postthermal treatment looked very similar.

(6) Series SSM

Figure 6 (bottom) shows the weight loss of selected SSM samples over the ranges RT-350°C, 350°C-750°C, 750°C-1000°C, and RT-1000°C. There was increased weight loss over the range RT-350°C (2.1%) compared to the nonground starting mixture (0.4%). The weight loss between 350°C and 750°C dropped from 5% in the starting mixture to 2.17% in the ground sample. Compared with the ESM series, the SSM series showed a higher degree of destruction of α -C₂SH, confirming the XRD and IR observations (Fig. 1). The thermally treated ground SSM samples showed the same trend as the corresponding ESM samples. Treatments above 300°C resulted in a much reduced weight loss over the range RT-350°C (0.1%-0.19%) compared to the SSMRT sample (2.1%). The samples treated at 370°C and 420°C showed a weight loss of 1.3% and 1%, respectively, over the range 350°C-750°C, similar to analogous ESM samples. The total weight loss to 1000°C was higher for the SSM series. This was due mainly to increased loss at 750°C-1000°C, through decomposition of carbonate. It seems that the SSM samples were thus more prone to carbonation.

In summary, grinding with SSM produced more CHSH than ESM. Both series show very similar thermal behavior producing C–CH–S at 380° C– 420° C. Subtracting the known contents of quartz (2 wt% from HP and 50 wt% from sand), calcium carbonate (1.4 wt%), and water yielded a dry mass of 42 wt% C–CH–S. From the total weight loss it was possible to calculate a specific water content of the C–CH–S of about 2.5 wt%. After treatment at temperatures above 420°C, ESM and SSM samples both contained Ca₂SiO₄ (C₂S), but in different polymorphic modifications.

(A) TMS: The degree of silicate polymerization was analyzed by the TMS method including trimethyl silylation and subsequent determination of the silicate species with chromatography (GC and LC). All samples gave similar measurable SiO₂ contents, of between 9.9 wt% and 11.2 wt %, consistent with the phase composition, and a reasonable yield of 70% to 80% (see experimental TMS). This implied that all changes in polymerization upon treatment remained measurable (i.e. the newly formed silicate species were not longer than pentamers).

There was a general increase in the number of dimers (Si_2O_7) after thermal treatment at temperatures above 340°C, compared to samples not treated or treated at lower temperatures (Fig. 7). The RT sample contained about 20 wt% of dimers, originating from the CHSH phase formed during milling and traces of amorphous remnants of the phase jaffeite from the hydrothermal product. Monomers corresponded to α -C₂SH and CHSH. Over the temperature range RT-320°C there were no significant changes in silicate polymerization.



Fig. 7. (a) Results of TMS of the products of the ESM series (double analysis, standard deviation <1%). The samples treated in the temperature range 340° - 400° show an increased proportion of dimeric silicate species. (b) Reproducibility tests with three different series labeled 56° C, 65° C, and 91° C thermally treated at 200°C (300°C), 400°C, and 460°C. TMS results show in all series the same trend: increase in the dimeric and trimeric portions of the silicate species in all samples heated at 400°C followed by depolymerization at 460°C.

Over the range 340°-400°, dimers form at the expense of monomers. Garbev et al. described a similar behavior of α -C₂SH as the phase transformation of α -C₂SH to dellaite, Ca₆[Si₂O₇][SiO₄](OH)₂, with partial polymerization of the silicate tetrahedra.¹⁷ The observed phase C-CH-S could therefore represent a mixture of partially dehydrated CHSH and a dellaite-like compound formed independently from α -C₂SH. Alternatively, amorphous C-CH-S may have formed as a homogenous phase, consisting of monomers and dimers. In fact, the increase in dimer content was quite small (approx. 10% of monomers polymerize). Thus, only approximately 1/3 of the α -C₂SH still present after milling could have transformed to a dellaite-like compound. As crystalline dellaite was not observed in XRD patterns, the polymerization must have occurred on a nanoscale not observable by XRD. Formation of dellaite may depend on some critical domain size of the original α -C₂SH crystals. Recent investigations of the transformation α -C₂SH– dellaite under similar conditions suggested the formation of an intermediate phase similar to killalaite, $Ca_{3+x}[H_{1-2x}Si_2O_7](OH)$.⁴⁰

The samples treated at 460°C and 500°C had a similar monomer to dimer ratio as those treated at 320°C, indicating that dimer formation was restricted to a small temperature range. Condensation could be suppressed by rapid heating through the critical temperature window, forming γ -C₂S and *x*-C₂S directly from α -C₂SH at higher temperatures, as evidenced by XRD. The amorphous C–CH–S phase stable over the range 360°C–400°C exhibited structural differences (in terms of crystallinity and silicate speciation) to both the starting materials (CHSH, α -C₂SH, monomeric, Q⁰) and to all known C₂S modifications (monomeric, Q⁰).

The silicate polymerization was further investigated by preparation of three additional series of samples with similar starting materials and similar mechanochemical treatment. TMS analyses after thermal treatment at three temperatures, 200°C or 300°C, 400°C and 460°C, showed analogous trends in terms of silicate species as a function of the treatment temperature (Fig. 7), supporting the considerations mentioned above.

(B) BET: BET measurements of the starting materials revealed a SSA of the hydrothermal sample equal to $8.3 \text{ m}^2/\text{g}$, whereas that of the quartz sand was about $0.7 (\pm 0.2) \text{ m}^2/\text{g}$ (Fig. 8). This corresponded to a SSA of the mixture of



Fig. 8. Specific surface area (BET). The hydraulically reactive samples have a SSA of about 2.7 m^2/g . HP—hydrothermal product (square), QS—quartz sand (triangle), ESMRT—ground sample.

4.5 m²/g. After grinding, a decrease in the SSA to 3.7 (± 0.3) m²/g was observed.

SSA decreased further upon thermal treatment to 2.7 m²/g at 360°C. In the stability range of amorphous C–CH–S (360°C–420°C), the SSA remained at 2.7 m²/g, whereas a further increase in temperature to 440°C–500°C led to a slightly higher SSA (3.0 m²/g). Ishida *et al.*¹⁰ observed a similar trend in the thermal behavior of α -C₂SH, which showed a higher surface area at RT-500°C (12.7–10 m²/g). In the work presented here, the grinding of the hydrothermal material with quartz resulted in "coarsening" of the particles and chemical reactions. In general, the differences observed were small and should not be over interpreted.

(7) IR Spectroscopy

Figure 9 shows the IR spectra of the hydrothermal product (HP) and its mixtures with quartz after grinding in the ESM mill and consequent thermal treatment in the range 300°C-500°C, whereas Table 1 shows the band assignments. The sample HP showed the typical bands for α -C₂SH¹⁷ [and references therein] at 675, 709 (OH–(Ca) librations), 757 (v_1 -Si–O(H)), 863, 943, 984 (Si–O stretching in SiO₄ tetrahedra), and 1281 cm⁻¹ (δ -OH). In addition, there were bands at 830 cm⁻¹ and 1054 cm⁻¹ belonging to jaffeite.^{41,42} The OH range was characterized by the sharp band at 3537 cm⁻¹ (v_1 -OH, α -C₂SH) and the broad bands centered at 2450 cm⁻¹ and 2850 cm⁻¹, typical for OH stretching of hydroxyl involved in strong H-bonding. The broad bands were split due to Fermi resonance interaction with δ -OH(Si) at 1282 cm^{-1,43,44} The hydrogen-bonding system interconnects the isolated SiO₄ tetrahedra in a chain-like pattern along the *b*-axis of α -C₂SH.⁴⁵ In addition, weak bands typical for v₁-OH of $Ca(OH)_2$ and jaffeite could be resolved at 3643 cm⁻¹ and 3624–3607 cm⁻¹, respectively.^{41,42,46} In the ground samples (ESMRT-ESM500), there were additional bands at 694, 778, 798, 1096, and 1172 cm^{-1} assigned to quartz. The

ground sample ESMRT, which was not thermally treated, showed features typical for Celitement materials of type CHSH including: (1) broad hump in the range of the antisymmetrical Si-O stretching (800-1000 cm⁻¹, marked with blue dotted line in Fig. 9); (2) splitting of the symmetrical Si-(OH) stretching vibration of α -C₂SH at 754 cm⁻¹ into two bands at 746 and 761 cm⁻¹; (3) bending vibrations typical for molecular water at 1610 cm^{-1} ; and (4) the presence of new H₂O environments in the OH stretching region. These IR features were in an excellent agreement with the thermal analysis results. In addition, the IR spectra of the ground sample and also of samples ESM300 and ESM320 were dominated by α -C₂SH bands, but broadened compared to those of HP, due to the reduction in crystallite size upon grinding. The water content in the CHSH phase of the Celitement type in the samples treated at temperatures >300°C was reduced. The samples treated at 340°C and 360°C (ESM340 and ESM360) also showed a strong reduction in the intensities of the α-C₂SH bands, which was more pronounced in the spectrum of the latter. Although there were no identifiable α -C₂SH silicate bands of in the spectrum of the sample treated at 360°C (ESM360), the OH region still possessed the band at 3537 cm⁻¹ indicating some preservation of the Ca–OH environments. This band existed in all samples treated thermally up to 420°C. At higher temperatures, the bands typical for hydrogen-bonded Si-OH were no longer present implying a destruction of the hydrogen-bonding system. Spectra of samples treated at 360°C, 380°C, and 420°C showed a broad band centered at about 935 cm⁻¹, due to the amorphous C-CH-S phase. Samples treated at temperatures above 440°C showed crystallization of C₂S polymorphs manifested by the occurrence of bands at 850, 916, and 987 cm⁻¹. Portlandite was evidenced by IR spectroscopy at temperatures up to 400°C, whereas jaffeite bands were discernible up to 420°C. The presence of a broad "H2O-hump" in the range 3100-3600 cm⁻¹ in the IR spectra of the samples heated between 380°C and 420°C supports unambiguously the TG results.



Fig. 9. IR spectra of the samples of the ESM series in the range $600-1700 \text{ cm}^{-1}$ (left) and $2200-4000 \text{ cm}^{-1}$ (right). HP—hydrothermal product. The dashed lines represent the shape of the A-band (see Table 1) in the spectra of α -C₂SH. The ground material shows broadening of the IR bands and occurrence of new H₂O environments corresponding to CHSH (highlighted with blue dotted line). The spectra between the arrows correspond to the amorphous cementitious material C–CH–S mixed with quartz. The broad band typical for this material is centered at about 935 cm⁻¹. Destruction of the H-bonding system as a result of the thermal treatment is shown by collapse of the bands at 2450 and 2850 cm⁻¹. The insert on the right-hand side shows the OH stretching bands of the minor components portlandite (P) and jaffeite (J) and the presence of "H₂O hump" marked with red dotted line in the spectra of the samples treated up to 420°C.



Fig. 10. Left: Heat flow of the products of the ESM series at RT and heated at 300°C, 320°C, 340°C, 360°C, 380°C, 400°C, 420°C, 440°C, 460°C, 480°C, and 500°C upon reaction with water as function of hydration time. Right: Total heat release (in J/g) after 70 h hydration. The heat release increases with increasing temperature of treatment. Maximum heat release is observed in the range 360°C–420°C. Sample ESM500 500°C shows completely different hydraulic behavior due to presence of anhydrous C_2S .

(8) Calorimetry

Specific heat release as a function of time upon hydration showed clear differences between the differently thermally treated ground materials (Fig. 10). In general, in the first few seconds after addition of water there was a sharp peak due to the wetting of surfaces and initial dissolution of highly soluble nanoparticles. After an induction period, characterized by a very low heat release, the hydration process, controlled by the precipitation of calcium silicate hydrates began. Hydration was characterized by an exponentially increasing heat flow which reached a maximum 5–5 h after addition of water. Finally, the heat flow decreased continuously, until reaching the asymptotic approximation of the line of zero heat release after 30–50 h.

There was a substantial increase in the heat flow (maximum at 3.8-4.4 mW/g) for samples treated in the range 360°C-420°C. Generally, thermal treatment shortened the dormant period, but there was no clear correlation. For example, the heat flow maximum of sample ESM300 was about 15 h, whereas that for sample ESM380 was 12 h. These features underscored the increased reactivity of the materials produced after treatment in the range 360°C-420°C. The total heat release after 70 h (Fig. 10, right) gave a maximum for samples treated in the same range. However, the sample heated at 500°C showed a completely different hydration behavior, with much lower heat flow (0.7 mW/g)and delayed reaction evidenced by a double maximum at 18 h and 24 h. The higher heat release of the samples treated between 380°C and 420°C could not be explained by considering their SSA, as BET results suggested a lower SSA.

All the materials used in this study (besides the starting materials in terms of hydrothermal product and quartz) form a C–S–H phase upon their reaction with H_2O independently of their pretreatment.

IV. Conclusions

A novel cementitious material referred to as C–CH–S, which is amorphous on the XRD scale, was produced via mechanical and thermal treatment of a mixture of SiO₂ (quartz) and hydrothermally synthesized calcium silicate hydrates (α -C₂SH and jaffeite). Its production is independent of the type of the mill used (SSM, ESM) after thermal treatment of the ground materials in the range 360°C–420°C. A typical feature with regard to the silicon anionic structure of this material is the increased silicate polymerization (up to 27% Si₂O₇ silicate species) as revealed by TMS. Infrared spectroscopy showed that the material is characterized by a very broad absorption band centered at 935 cm⁻¹. Another typical feature is the presence of about 2.5% water, which is present as hydroxyl groups in Ca–OH species as shown by TG and confirmed by IR spectroscopy. The hydrogen-bonding system characteristic for both phases present in the material prior to thermal treatment, α -C₂SH, and an amorphous calcium hydrosilicate hydrate of the Celitement type, is completely destroyed upon treatments at 360°C and higher. Calorimetric measurements indicate a very high hydraulic reactivity of this cementitious material, which is beyond that which is typical for C₂S-like materials.

Technology transfer beyond the laboratory scale seems feasible given the availability of large autoclaving systems used in the production of aerated concrete. The grinding is an integral part of every cement plant and the heating temperatures needed could be easily provided by industrial waste heat. This concept is already partly realized in the Celitement pilot plant at Karlsruhe, Germany.

An interesting phenomenon is the formation of different dehydration products at temperatures higher than 440°C depending on the type of mill used. The more intense treatment by using SSM possibly leads to formation of β -C₂S-like domains in the amorphous structure stabilized by OH, which upon thermal treatment at higher temperatures (T > 440°C) are easily transformed in α '_L-C₂S.

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