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: \( \alpha\)-Ca₂[HSiO₄](OH) (\( \alpha\)-C₂S-H) and \( \alpha\)[SiO₄] (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 \( \sim\)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-oxide–hydroxide–silicate (C–O–H–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 \( \alpha\)-C₂S upon its transformation into water-free Ca₂SiO₄ modifications is discussed.

I. Introduction

Efforts 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 \( \beta\)-C₂S and \( \gamma\) with different dopants is one key issue in this case. Excellent reviews of this topic have been written by both Chatterjee\(^{12}\) and Gartner.\(^{13}\)

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. However, several variations of this approach are described in literature, differing mostly in the starting materials, e.g., fly ash\(^{1–7}\) 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 \( \alpha\)-Ca₂[HSiO₄](OH) (\( \alpha\)-C₂S-H) as a crystalline calcium silicate hydrate precursor (with a few exceptions on a laboratory scale where hillebrandite, \( \alpha\)[SiO₄] (OH)₂, was synthesized)\(^{11–14}\) and (2) the cementitious material resulting from the subsequent thermal treatment (300°C–1000°C) is always a crystalline Ca₂SiO₄ polymorphic modification: \( \beta\)-C₂S, \( \gamma\)-C₂S, or \( \gamma\)-C₂S. As the thermal behavior of the precursor (in this case \( \alpha\)-C₂S) 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 \( \alpha\)-C₂S, and furthermore there is an even greater discrepancy concerning the resulting polymorphs of Ca₂SiO₄\(^{10,15,16}\). 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 \( \alpha\)-C₂S-H, jaffeite, \( \alpha\)[SiO₄] (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 Exzentermühle (ESM) and Scheibenmühle (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 REACTOR AG (Lengnau, Switzerland) with permanent stirring. The volume of the autoclave is 3 l 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 vibration mill, ESM (SIEBTECHNIK, Mülheim/Ruhr, Germany) for 4 h. The sample produced in this way was labeled ESMRT. This synthesis corresponds to the “Celite” 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 1000 g hydrothermal product was ground together with 1000 g quartz sand (96 wt% quartz) in an eccentric vibration mill, ESM (SIEBTECHNIK, Mülheim/Ruhr, Germany) for 4 h. The sample produced in this way was labeled ESMRT. This synthesis corresponds to the “Celite” 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 200°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, Osnaabrück, 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 methods, and calorimetry. Because of the limited scale-up 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 PIXcell detector (255channels, 3.347°2θ) and Cu-radiation. The CuKα was filtered with Ni-filter. The measurements were taken with colder slits 0.4 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.27 Silicaids (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 ±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)12Si6O18: 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 GLOBAR source and MCT detector. Spectra were taken in the range 600–4000 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/p0: 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
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 \(\alpha\)-C\(_{2}\)SH as the main constituent (67 wt\%), with 7 wt\% Ca\(_6\)[Si\(_2\)O\(_7\)](OH)\(_6\) (jaffeite), 3.8 wt\% quartz, and negligible quantities of portlandite and CaCO\(_3\) (calcite). XRD showed about 19 wt\% amorphous content. Figure 1 (left) shows the phase composition of the hydrothermal product (HP), mixture HP+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 \(\alpha\)-C\(_{2}\)SH (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 \(\alpha\)-C\(_{2}\)SH 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 \(\alpha\)-C\(_{2}\)SH 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 C\(_2\)S polymorphic modifications, \(\alpha\)-C\(_{2}\)S and \(\gamma\)-C\(_{2}\)S, became visible in the XRD patterns. With further increases in temperature, increasing amounts of these crystalline C\(_2\)S 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 \(\alpha\)-C\(_{2}\)SH (Fig. 1). The quantitative analysis pointed to a higher degree of grinding-induced amorphization than that for the ESMRT sample, leading to almost 45 wt\% amorphous component. Correspondingly, the quantity of \(\alpha\)-C\(_{2}\)SH decreased to 11 wt\%. The amorphization of quartz was of a similar order (6\%) to...
Therefore, in both series, an amorphous phase appeared to form, which mostly originated from the main components of the hydrothermal product $\alpha$-$\mathrm{C}_2\mathrm{SH}$ and jaffeite. This phase has already been described as an amorphous CHSH of Celitement type,\textsuperscript{18-22} which is characterized by the presence of about 5\% H$_2$O as both OH groups and molecular H$_2$O. The molecular H$_2$O is formed by partial hydrolysis and condensation of OH groups. The OH groups are bound to both Ca and Si. Partial polymerization of monomeric SiO$_4$ tetrahedra to dimeric Si$_2$O$_5$ and even higher polymeric silicate species also takes place as a result of grinding.

Obviously, another amorphous phase (with considerably reduced H$_2$O content) was formed in the temperature range 370°C–420°C due to the reaction and dehydration of $\alpha$-$\mathrm{C}_2\mathrm{SH}$ and the amorphous CHSH of the Celitement type which was present at RT. This amorphous product transforms into $\mathrm{C}_2\mathrm{S}$ at temperatures above 420°C. There is an obvious discrepancy regarding the temperature of dehydration of $\alpha$-$\mathrm{C}_2\mathrm{SH}$ between the results from the TA and \textit{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 Ca$_2$SiO$_4$ (C$_2$S) in addition to quartz, but the C$_2$S polymorphic modifications were different. In the case of the ESM series, there was formation of $\gamma$-$\mathrm{C}_2\mathrm{S}$ and $\alpha$-$\mathrm{C}_2\mathrm{S}$, whereas in the SSM series $\gamma$-$\mathrm{C}_2\mathrm{S}$ 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 $\alpha$-$\mathrm{C}_2\mathrm{SH}$ that point to a rather complicated and unpredictable dehydration mechanism. Different authors show formation of $\gamma$-$\mathrm{C}_2\mathrm{S}$,\textsuperscript{27,28} $\alpha$-$\mathrm{C}_2\mathrm{S}$,\textsuperscript{10} $\beta$-$\mathrm{C}_2\mathrm{S}$,\textsuperscript{29,30} or dellaite.\textsuperscript{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 $\gamma$-$\mathrm{C}_2\mathrm{S}$ at temperatures as low as 440°C, although this polymorphic modification is normally known to be stable at higher temperatures (675°C–1177°C).\textsuperscript{31-33} Together with $\beta$-$\mathrm{C}_2\mathrm{S}$ and $\mathrm{C}_4\mathrm{A}_3$ (yellinite), $\gamma$-$\mathrm{C}_2\mathrm{S}$ is one of the most abundant phases in belite sulfoaluminate cements that are burned at temperatures some 200°C lower than portland cement.\textsuperscript{34,35} Alpha$\gamma$-$\mathrm{C}_2\mathrm{S}$ is normally stabilized by the presence of impurities, e.g., MgO.

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K₂O, BaO, and SO₃ or Na₂B₄O₇·10H₂O (borax). Kacimi et al. reported the synthesis of α-C₂S from fly ash with hydrothermal pretreatment at temperatures as low as 800°C. Formation of a poorly crystalline β-C₂S was reported after grinding of pure α-C₂SH in an SSM mill at RT. The authors described the formation of well-crystalline β-C₂S after thermal treatment of the ground material at 400°C and of α’-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 α’-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 Roy 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. 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 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 and is typical in the
H2O content in these samples. The total weight loss over the

tive determinations by IR spectroscopy revealed 0.9–
TG curves of the samples heated to 380
°
°
temperatures above 650
decarbonation. In addition, there was no dehydroxilation at
event at about 840
(seen as two broad “humps” in Fig. 5, top) and a sharp
formation of cementitious amorphous CHSH of the Celite-
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 \( \text{CO}_2 \) 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 treat-
ment 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. Quantita-
tive 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 amor-
phous \( \text{CaCO}_3 \) 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 \( \text{Ca-OH} \) linkages (see
IR) \( \text{CaO-Ca(OH)_2-SiO}_2 \) [C–CH–S].
The CO\(_2\) 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 \( \text{CaCO}_3 \) 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 amorhization 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 non-
ground 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 \( \pi\text{-C}_2\text{SH} \), confirming the XRD and IR observations
(Fig. 1). The thermally treated ground SSM samples showed
the same trend as the corresponding ESM samples. Treat-
ments 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 sam-
ple. 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 \( \text{C–CH–S} \) 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\% \( \text{C–CH–S} \). From the total weight loss it was possible
to calculate a specific water content of the \( \text{C–CH–S} \) of
about 2.5 wt\%. After treatment at temperatures above
420°C, ESM and SSM samples both contained \( \text{Ca}_2\text{SiO}_4 
(\text{C}_2\text{S}) \), 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 SiO\(_2\) 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
(\( \text{Si}_2\text{O}_7 \)) 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
\( \pi\text{-C}_2\text{SH} \) and CHSH. Over the temperature range RT–320°C
there were no significant changes in silicate polymerization.
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. 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, Ca₃⁺x[H₁−₂xSi₂O₇](OH). 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 α-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 m²/g, whereas that of the quartz sand was about 0.7 (± 0.2) m²/g (Fig. 8). This corresponded to a SSA of the mixture of...
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. observed a similar trend in the thermal behavior of α–C–SH, which showed a shift of the bands and occurrence of new H₂O environments corresponding to CHSH (highlighted with blue dotted line). 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–C–2SH [and references therein] at 675, 709 (OH–(Ca) librations), 757 (ν1–Si–O–(H)), 863, 943, 984 (Si–O stretching in SiO₄ tetrahedra), and 1281 cm⁻¹ (ν3–OH). In addition, there were bands at 830 cm⁻¹ and 1054 cm⁻¹ belonging to jaffeite. The OH range was characterized by the sharp band at 3537 cm⁻¹ (ν1–OH, α–C–SH) 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. The hydrogen-bonding system interconnects the isolated SiO₄ tetrahedra in a chain-like pattern along the b-axis of α–C–2SH. In addition, weak bands typical for ν1–OH of Ca(OH)₂ and jaffeite could be resolved at 3643 cm⁻¹ and 3624–3607 cm⁻¹, respectively. In the ground samples (ESMRT–ESM300), 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 anti-symmetric 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–C–2SH 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–C–SH 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–C–2SH bands, which was more pronounced in the spectrum of the latter. Although there were no identifiable α–C–2SH silicate bands 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 cm⁻¹ (left) and 2200–4000 cm⁻¹ (right). HP—hydrothermal product. The dashed lines represent the shape of the A-band (see Table 1) in the spectra of α–C–2SH. 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.
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 a 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 C₃S.

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 H₂O 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 (C₃S_H 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 C₄–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, C₄–SH, and an amorphous calcium hydroxysilicate hydrate of the Cenitement 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 C₃S-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 Cenitement 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 C₂S_H.

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References


(8) Calorimetry

Calorimetric measurements indicate a very high hydraulic reactivity of this cementitious material, which is beyond that which is typical for C₃S-like materials.