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Reactivity and phase composition of Ca_2SiO_4 binders made by annealing of alpha-dicalcium silicate hydrate

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ABSTRACT

This study investigates the production of highly reactive dicalcium silicate Ca_2SiO_4 (C_2S).
To that end, binders were synthesised by annealing of alpha-dicalcium silicate hydrate (α-C_2SH) between 400 and 800 °C. Two different heating sequences were tested. The phase compositions were determined by means of XRD. Depending on the annealing temperature and the heating conditions the cementitious materials consist of an X-ray-amorphous content as well as x-Ca_2SiO_4 (x-C_2S) and γ-Ca_2SiO_4 (γ-C_2S). The hydration kinetics of some selected binders were investigated by means of isothermal calorimetry. The specific reactivity of the phases produced by means of annealing was determined during the first 40 h of hydration by use of XRD and TGA.
The resulting binders show the highest reactivity when low annealing temperatures (<500 °C) were used. After 72 h, degrees of hydration of about 89% are achieved. The most reactive component is the X-ray-amorphous content, followed by x-C_2S.

1. Introduction

The manufacturing of cement is energy-consuming and is responsible for about 8% of anthropogenic CO_2 emissions [1]. Since the early seventies, reactive belite cements were developed to reduce the clinker factor and the energy consumption during manufacturing [2]. However, Chatterjee [3,4] reported that these high temperature techniques may not lead to the desired conservation of energy.

Since about two decades alternative lab scale routes to producing highly reactive belite binders at lower temperatures ($\ll$1400 °C) are progressively being investigated.

Several chemical approaches like sol–gel synthesis [4–6] and Pechini process [7] were reported, but those techniques are mainly used for the production of phase-pure C_2S for research. A possible upscaling to industrial manufacturing seems to be limited because chemical reagents like $Ca(NO_3)_2$ are required.

Another more promising approach is the hydrothermal processing followed by thermal activation.

Jiang and Roy [8] and later Guerrero and co-workers [9–11] used fly ash and CaO as raw materials to produce fly ash cement, respectively fly ash belite cement (FABC). Hydrothermal processing was carried out at 200 °C for 4 h, the thermal activation was conducted between 700 and 900 °C. Resulting binders typically consisted of α'_L-Ca_2SiO_4 (α'_L-C_2S), β-Ca_2SiO_4 (β-C_2S), calcium aluminates and calcium silicate aluminates. The hydraulic activity of such binders seems to be moderate. Measurements of Guerrero [9] show heat releases of 30–80 J/g after hydration of 24 h. The mechanical strength appears to be very low. Results from mortars which were prepared with a very high w/b value (1.05–1.5) achieved only 0.3–11.4 MPa after 7 days [12].

Yet another approach is the targeted synthesis of hillebrandite ($Ca_2(SiO_3)(OH)_2$) or α-C_2SH ($Ca_2[HSiO_4](OH)$) during hydrothermal process. Hillebrandite is an orthorhombic inosilicate [13] which is difficult to obtain by hydrothermal treatment at temperatures usually between 150 °C and 250 °C [14]. Ishida [15] reported that decomposition starts at temperatures of about 500 °C and produces low-crystalline β-C_2S. Hydration of such binders is supposed to be relatively fast. It is reported that a β-C_2S binder prepared at 600 °C is completely hydrated after 28 days (water/solid = 0.5, 25 °C) [16].

Alpha-dicalcium silicate hydrate is an orthorhombic nesosilicate and can be easily produced by means of autoclaving between 95 and 200 °C [14]. Dehydration was investigated by several authors resulting in different phase compositions of dehydrated material. Heller [17] and Butt [18] reported that after annealing at 500 °C only γ-C_2S was detected. They could not determine if γ-C_2S is the initial product of dehydration or if it results from decomposition of preliminarily formed β-C_2S. Jernejcic [19] later confirmed the formation of γ-C_2S as initial product by in situ XRD measurements at 500 °C.

Ishida [20] reported that the dehydration of α-C_2SH starts at temperatures between 390 and 490 °C and produces γ-C_2S and an intermediate phase. This intermediate phase is a new type of dicalcium silicate which Miyazaki [21] later named x-C_2S. His designation is also used in this article. The crystal structure was described by Toraya [22]. The

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formation of x-C_2S was also observed by Garbev and co-workers [23] who investigated the dehydration of three different samples of α-C_2SH. In addition they reported the formation of dellaite ($Ca_6[Si_2O_7][SiO_4](OH)_2$) at temperatures between 290 and 620 °C in two samples. Gamma-C_2S was not observed.

In situ XRD [19,20,23] shows that heating of α-C_2SH above 790–960 °C transforms the material into α'_L-C_2S which converts to β-C_2S after cooling to room temperature.

The production of belite binder by thermal dehydration of α-C_2SH between 500 and 1000 °C is already patented [24].

However, only little information about reactivity of thermally activated α-C_2SH is reported. Ishida [20] found that x-C_2S produced at 500 °C hydrates completely in 24 h at 25 °C (water/solid = 1.0) whereas γ-C_2S reacts only slowly. Dellaite is considered to possess no hydraulic activity. Binders activated at 600–1000 °C are described to be as sluggish in reaction as material which is produced in a rotary kiln [25].

Because of the possibility of low calcination temperatures and the expected high hydraulic activity of x-C_2S, the thermal activation of α-C_2SH seems to be a beneficial way to produce highly reactive C_2S binder with an improved CO_2 footprint. Therefore this study focuses on the lab scale synthesis of reactive C_2S binders by means of this route. Because of low energy consumption and high expected hydraulic activity this study focuses especially on low calcination temperatures. The differences in reported phase composition of annealed material are supposed to be clarified, with particular emphasis on the contents of γ-C_2S and x-C_2S. Therefore the influence of heating conditions and annealing temperatures in the range of 400–800 °C on phase composition will be determined. Reactivity will be investigated by comparison of calorimetric measurements, phase composition and phase decomposition during the hydration process.

2. Materials and methods

Alpha-dicalcium silicate hydrate was synthesised by mixing $Ca(OH)_2$ (p. a., Roth, Germany) and highly dispersive SiO_2 (p. a., Merck, Germany). The molar ratio was $Ca(OH)_2/SiO_2 = 2$. Prior to the synthesis, 5% α-C_2SH seeds were added. Solids were suspended in de-ionised water (water/solid = 10) and autoclaved in a 700 ml stainless steel vessel (BR700, Berghof, Germany) at 200 °C for 16 h. During the autoclaving process, the suspension was stirred at 200 rpm. The resulting α-C_2SH was filtered and dried at 80 °C.

In order to determine the quantitative phase composition of α-C_2SH, the produced binders as well as the hydrated samples were investigated by means of powder X-ray diffraction (XRD). XRD experiments were carried out with a Siemens D5000 diffractometer (Bragg–Brentano geometry, energy-dispersive Sol-X detector) operating with copper radiation at 40 kV and 40 mA. The scanning was performed at a step width of 0.02° 2θ over an angular range from 12 to 90° 2θ with 6 s counting time per step. The external standard method [26,27] was used for the quantification of the phase composition including X-ray-amorphous contents. Zincite (ZnO) was used as external standard. The required scale factors, the density and the volume of the unit cells of the relevant phases were calculated by AutoQuan (Version 2.7.0.0, Agfa NDT Pantak Seifert GmbH co. KG).

The mass absorption coefficients (mac) of the samples were calculated from [28], based on the chemical formulae of the present sample. The CaO and SiO_2 contents were known from the initial weights. The CO_2 and H_2O contents were determined by TGA. As the mac of H_2O (10.2 cm^2/g) and CO_2 (9.6 cm^2/g) are very similar, an imprecise quantification of calcite by TGA/DSC will result in a very low error of determined phase composition. Simultaneous TGA/DSC was carried out deploying an SDT Q600 manufactured by TA Instruments, New Castle, DE, USA. The measurement was performed in the temperature range of 25–1000 °C with a heating rate of 10 K/min under N_2 flux (100 ml/min).

Synthesised α-C_2SH was investigated by high-resolution Environmental Scanning Electron Microscope with Field Emission Gun (ESEM-FEG, XL30, FEI/Philips) at the following conditions: temperature = 12 °C, water vapour pressure = 9.8 Torr, Gaseous Secondary Electron Detector (GSED), and acceleration voltage = 25 kV.

Binders were produced by thermal dehydration in a muffle furnace (Linn, Germany) in air. 5 g of α-C_2SH was filled in a platinum crucible and heated at different temperatures using two heating sequences A and B. The investigated annealing temperatures ranged between 400 and 800 °C. In series A the samples were put in the preheated oven (400, 412, 420, 450, 475, 500, 600 and 800 °C) for 1 h. The corresponding samples are labelled “A” in the text, followed by the annealing temperature. In series B, the samples were put in the hot furnace at 420 °C for 1 h. Subsequently, they were heated up to the desired temperature (450, 475, 500 and 800 °C) and held there again for 1 h. Those samples are labelled “B” with the addition of the final annealing temperature.

BET specific surface area of α-C_2SH and binder series A was determined by N_2 adsorption (SA 3100, Beckmann Coulter, Brea, CA., USA).

In order to characterise the hydration process, the heat release of the dehydrated α-C_2SH was monitored by means of isothermal heat conduction calorimetry at 20 °C (ToniCal Trio, Toni Technik, Berlin, Germany). The water/solid-ratio used was 2 due to the high fineness of materials. Measurements were carried out over 72 h. In addition, during the first 40 h, the hydration of binder A420 was investigated by quantitative XRD and TGA/DSC analyses. For that, 4 samples of A420 were prepared using deionised water with a water to solid ratio of 2 and stored in a sealed PE container at 20 °C and 65% relative humidity. The hydration was stopped by fast drying at 45 °C on a pre-heated brass plate after 2, 12, 19 and 40 h. For the calculation of quantitative phase composition from XRD, the dilution of the samples due to bond water was taken into account by the following formula.

$$\frac{\text{phase content QXRD}}{100} \cdot (100 + \text{loi}) = \text{phase content after hydration} \quad (1)$$

Newly formed portlandite was quantified by both TGA and XRD. Therefore, the characteristic weight loss between 400 °C and 450 °C was attributed to $Ca(OH)_2$. The superposed weight loss of C-S-H was taken into account by extrapolating slopes before and after weight loss of portlandite.

3. Results

3.1. Alpha-dicalcium silicate hydrate

The composition of the synthesised α-C_2SH determined by Rietveld QXRD analysis showed 89% α-C_2SH (ICSD 75277), 3% calcite $Ca(CO_3)$ (ICSD 100676), 4% scawtite $Ca_7[Si_6O_{18}](CO_3)\cdot 2H_2O$ (ICSD 2502) and 4% X-ray-amorphous material (see Fig. 1). The SEM investigation (Fig. 2) shows interlocked rectangular plates. TGA/DSC analysis is shown in Fig. 3. The total weight loss was determined to be 10.82%. This coincides approximately with the total mass loss of 10.1% calculated from the phase composition determined by XRD (8.4% from α-C_2SH, 1.32% from calcite and 0.38% from scawtite). An accurate quantification of the calcite and scawtite contents by TGA/DSC is not possible for this sample because calcination processes cannot be separated exactly from each other. In the typical temperature range for calcite decomposition of 750–850 °C [29], no drop in the mass loss curve and no endothermic heat flow peak are detected. However, it is supposed that main calcite calcination takes place between 620 and 650 °C where a drop in mass loss and an endothermic heat effect is observed. From cement manufacturing it is known that the decarbonation temperature of calcite can be shifted to this temperature range if it is intimately mixed with material which can react with CaO [30]. Scawtite is difficult to identify by TGA because only little information about thermal decomposition is available. Marincea [31] reported that a natural sample of