



Early hydration of C_2S doped with combination of S and Li

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Abstract

Production of low-energy cements would result in energy saving and lower CO_2 emissions related to reduced consumption of fuel and high-grade limestone as a raw material. Belite rich clinker, made more reactive by doping with combination of S and Li, could possibly be one of the low-energy alternatives for Portland cement clinker. Paper describes the preparation of doped belite and deals with its early hydration and reactivity. Belite rich clinkers were prepared in laboratory in high-temperature solid state synthesis. Pure substances were used for the preparation of raw meal and clinker. Early hydration heat flow development of cement pastes was monitored by isothermal calorimetry, changes in phase composition by “in situ” X-ray diffraction and TGA/DTA and microstructure by SEM-SE. Heat flow exotherms were correlated with quantified phase composition at given time. Intensity and position of main exothermic peak related to hydration of C_3S is changing with increasing Li content. Doping of the C_2S by the S or the combination of S and Li significantly increases the reactivity of the C_2S -rich cement. The formation of C–S–H products is a continuous process that depends mainly on C_3S during first 6 h and then is supported by slow reaction of β - C_2S . The reactivity of C_2S is affected by the timing of the hydration of other clinker phases. Two generations of portlandite formation detectable as a double endotherm on TGA/DTA can be attributed to hydration of C_3S and β - C_2S .

Keywords Belite clinker · S · Li · Doping · Early hydration

1 Introduction

The manufacture and use of concrete produce a wide range of environmental and social consequences. The cement industry is together with the energy production and transportation industries one of the three primary producers of carbon dioxide, a major greenhouse gas. The share of cement production in total anthropogenic CO_2 emissions has been rising steadily and is now estimated by some sources to be around 10% [1], or about 6% of the total anthropogenic greenhouse gases [2].

Although energy use and release of CO_2 are closely related in the usual cement manufacturing industry, it is the release of CO_2 to the atmosphere rather than the consumption of energy which is of chief concern. Decarbonation of limestone ($CaCO_3$) results in the release of CO_2 and,

since natural limestone and chalk are the only large-scale sources of calcium available to the cement industry, this CO_2 release is only reducible by changing the chemical composition of the cement [3].

Clinker is the main constituent of the cement. The clinker is mixed with a few per cent of gypsum and finely ground to make the cement. The clinker typically has a composition in the region of 67% CaO, 22% SiO_2 , 5% Al_2O_3 , 3% Fe_2O_3 and 3% of other components, and normally contains four major phases, called alite (C_3S , Ca_3SiO_5), belite (C_2S , Ca_2SiO_4), aluminat phase (C_3A , $Ca_3Al_2O_6$) and ferite phase (C_4AF , Ca_2AlFeO_5). Several other phases, such as alkali sulfates and calcium oxide, are normally present in minor amounts [4].

Recently, there are four classes of alternative clinker system that deserve serious attention with respect to global

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reductions in concrete-related CO₂ emissions [5]; reactive belite-rich Portland cement clinkers (RBPC), belite-ye'elimite-ferrite clinkers, carbonatable calcium silicate clinkers, magnesium oxides derived from magnesium silicates.

RBPC belong to the same family as ordinary Portland cement (OPC) in terms of clinker mineralogy, i.e. they are in the C₂S–C₃S–C₃A–C₄AF system. The difference in clinker composition between RBPC and OPC lies mainly in the belite/alite ratio. For RBPC the belite content is more than 40% and alite normally less than 35%, making belite the most abundant phase in RBPC, as opposed to alite in OPC. The manufacture of RBPC therefore leads to lower specific energy consumption and CO₂ emissions, and also has the additional practical advantage of requiring less high-grade (low-silica) limestone as a raw material [5]. The ideal clinkering temperature for RBPC is usually close to 1350 °C, which is about 100 °C lower than the average for OPC, which can lead to somewhat lower kiln heat consumption and permit more use of low-grade kiln fuels.

Physical or chemical activation, e.g. rapid clinker cooling or minor element doping may be needed in some cases to make the belite sufficiently reactive. As an example, the use of 0.5–1.0% SO₃ in the raw meal combined with rapid clinker cooling can lead to the formation of reactive belite in the clinker. Staněk and Sulovský [6] reported the principle of activation during preparation of belite-rich clinkers with an increased Ca:Si ratio in the structure of dicalcium silicate and partial substitution of SiO₄⁴⁻ by SO₄²⁻. Activation was realized by the addition of sulfate ions, which in the structure of belite substitute SiO₄, caused an increased entry of Al₂O₃ into the belite and increased the CaO:SiO₂ in belite. The sulfur addition to the clinker also stabilized the hydraulically more active monoclinic alite M1 modification. The clinker for its preparation, contained only around 20 wt% of alite, was burned at a temperature of 1350 °C and was activated by the addition of about 5% SO₃ (related to the bulk clinker weight). It contained a small proportion of anhydrite.

Specific kiln fuel requirements and CO₂ emissions of RBPC are typically about 10% below those for OPC. Lower emissions of NO_x and SO_x are commonly observed when making RBPC, due mainly to the lower burning temperature. On the other hand, it requires about 5% more electric power to grind RBPC to the same fineness as OPC, due to the greater hardness of belite relative to alite [5].

Pure C₂S exhibits five polymorphic forms, depending on temperature and pressure during formation [7], all are metastable except the γ (orthorhombic) form. In Portland cement the equilibrium temperature between α (hexagonal) and α' is 1280 °C and the conversion reaches a maximum rate at 1100 °C. With decreasing cooling rate, the α_H' (orthorhombic)

phase tends to dominate, and finally the belite is composed entirely of this form, which transforms into β-C₂S (monoclinic) after passing through the α_L' (orthorhombic) form [8].

Belite is a major phase in active belite cements and is chiefly present in the α and α' modifications, stabilized either by rapid cooling in the temperature range 1300–900 °C [8], or by the use of higher alkali levels [9]. It has been suggested that the hydraulic activity of β-C₂S is related to the calculated strength of the Ca–O ionic bond [10]. A study of the relationship between crystal structure and hydraulic activity, including synthetic β-C₂S and samples separated from Portland cement, indicates that the electric field strength at the site of the Ca²⁺ ions in the crystal lattice determines the hydraulic activity [11].

Recently, the Li battery production is growing. Since the proposed Li battery recycling solutions are not economically meaningful at present, there is a possibility of using Li waste in limited amounts in the cement industry as a raw material component for clinker burning in rotary kilns. Unlike sodium and potassium, Li forms non-volatile oxides at elevated temperatures in a rotary kiln. [12]. Lithium salts accelerate the hydration process of both Portland cement [4, 13] and calcium sulfoaluminate cements [14]. Li₂CO₃ addition decreases the decomposition temperature of CaCO₃ and lowers the formation temperature of β-C₂S and C₃S [15]. Li₂O can positively lower the free lime content after burning under the same defined conditions [16]. Kolovos et al. [17] revealed by SEM that addition of Li₂O strongly affects the clinker microstructure, specifically the size and shape of belite grains. The large alite crystals and belites of fish bone habit were observed. Li oxides easily form eutectic mixtures with SiO₂. Small amounts of lithium oxide improve the reactivity of the raw mix by lowering the melt formation temperature [12, 18].

Paper deals with early hydration of reactive C₂S-rich clinkers doped with a combination of S and Li. This combination of dopants hasn't been studied on belite clinker yet. Early hydration properties of cements prepared from the clinkers were monitored by isothermal calorimetry, XRD-in situ and inner standard method, DTA–DTG and SEM-SE. Paper brings comparison of reactivity and phase development during early hydration of S and Li doped belite clinkers and undoped belite clinker.

2 Methodology

2.1 Materials

Belite clinkers, prepared by high-temperature solid state synthesis, were doped with S and combination of S and 2% or 4% of Li in form of CaSO₄·2H₂O and LiCO₃.

Table 1 Raw meal composition for clinker preparation

	C ₂ S wt%	C ₂ S S	C ₂ S S 2Li	C ₂ S S 4Li
CaCO ₃	75.41	74.98	72.34	69.70
SiO ₂	24.59	21.16	21.16	21.16
LiCO ₃	–	–	3.66	7.32
CaSO ₄ ·2H ₂ O	–	3.86	3.86	3.86

Table 2 Phase composition of burned clinkers

	C ₂ S wt%	C ₂ S S	C ₂ S S 2Li	C ₂ S S 4Li
β-C ₂ S	27.1	42.5	80.7	82.5
γ-C ₂ S	72.7	27.3	1.0	1.1
C ₃ S	–	27.7	9.9	2.9
CaO free	0.2	2.5	7.7	10.0
Anhydrite	–	–	0.7	3.5

Pure compounds were used to prepare the clinkers. The composition of the raw meal constituents was calculated on the composition of belite. The raw meal composition and phase composition of burned clinkers are given in Tables 1 and 2. Raw meals were weighed into plastic bottles and homogenized in 3D motion homogenizer (Turbula) for 150 min. Then, the tablets were prepared and burned in Kanthal furnace at 1400 °C with 12 h of soaking time. Thereafter, the clinkers were quickly cooled in the air when they were placed on a metal substrate after being removed from the furnace. Cements were prepared by grinding the clinkers without gypsum on the fineness ~400 m²/kg (Blain). For isothermal calorimetry, X-ray and DTA testing, clinkers were ground in a vibratory mill for 1 min.

2.2 Methods

The development of heat flow and total hydration heat was monitored by isothermal calorimetry (TAM Air-TA Instruments) on samples of cements prepared from synthesized clinkers. Calorimetric measurements were performed at 25 °C for 7 days on cement pastes with w/c=0.4 when 5 grams of cement was used for individual test. Samples were stored under laboratory conditions at 25 °C for 24 h prior to the experiment. Before inserting the ampoules pastes into the calorimeter, each cement sample was mixed with water and stirred at 2 rpm for 1 min outside the calorimeter. The measurement itself started 1 min after the addition of the mixing water.

The in situ X-ray diffraction analysis was performed on Bruker D8 Advance apparatus with Cu anode ($\lambda K\alpha = 1.54184 \text{ \AA}$) and variable divergence slits at $\Theta-\Theta$ reflection Bragg–Brentano para focusing geometry, scan range 7–50 2Θ , scan step size 0.039°. Data were processed using EVA software. The duration of individual scans was approximately 20 min; duration of the whole experiment was 24 h. The paste (w/c = 0.4) was placed in a sample holder and covered with kapton foil to prevent carbonation. In case of C₂S S 2Li sample, the phase composition over time (0, 45, 90, 360, 720 and 2880 min) was monitored using the inner standard method. As a standard, 20 wt% fluorite was used. After each time interval the hydration was stopped by isopropyl alcohol and acetone.

The phase composition of burned clinkers was determined using Rietveld refinement. Since the inner standard method wasn't used the amorphous content was not quantified (Table 2).

The sample C₂S S 2Li was investigated by thermal analysis. The samples were prepared following the same procedure as for XRD. The hydration process of the paste was stopped by isopropyl alcohol and acetone after 45, 90, 360, 720 and 2880 min of hydration. Combined TGA/DTA data were obtained using STA 449 F3 Jupiter (by Netzsch). The samples were tested in Pt crucibles at a heating rate 10 °C/min, from 35 to 1000 °C. The sample atmosphere was synthetic air (50 ml/min, ratio N₂/O₂ was 80/20).

Development of microstructure at 45, 90, 360, 720 and 2880 min of hydration of the sample C₂S S 2Li was observed by scanning electron microscope ZEISS EVO LS10 in secondary electrons (SE). SE micrographs were taken at 100×, 500×, 1000×, 2000× and 5000× magnification, EHT 15 kV, WD 12 mm and I probe 80 pA. Samples were sputtered with gold before SEM SE analyses.

3 Results and discussion

3.1 Isothermal calorimetry

Early hydration exothermic reactions were monitored by isothermal calorimetry during 7 days of hydration (Fig. 1). Exothermic reactions are related to dissolution of amorphous and crystalline phases (Table 2), growth, nucleation and precipitation, complexation and adsorption processes. Main contributors of the evolved heat during hydration are portlandite–Ca(OH)₂ (CH) and C–S–H. These phases are hydration products of clinker phases C₃S and C₂S and CaO. Understanding the mechanism of cement hydration involve the study of the kinetics of individual mechanistic steps [19].

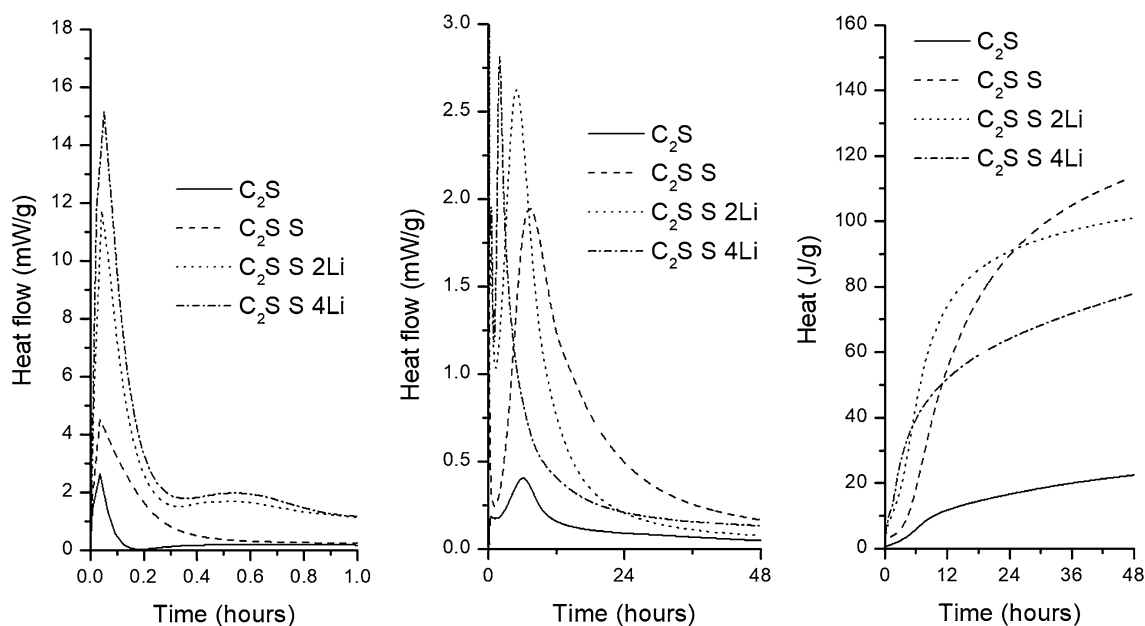


Fig. 1 Heat flow (1 and 48 h) and total heat (48 h) development

When in contact with water, the initial reactions' exotherms include wetting and dissolution/dissociation of molecular units from the surface of a solid. Despite the fact that the measurement started after 1 min after water addition, the first exotherm is still controlled by CaO content in the sample. Total heat evolved in the time interval between 1st and 60th min of hydration is proportional to CaO content in the samples (Table 2): C₂S—1.1 J/g, C₂S S—3.4 J/g, C₂S S 2Li—9.2 J/g, C₂S S 4Li—11.4 J/g. The CaO reaction during initial period of hydration exhibits large signal overshadowing other reactions. Samples with Li contains also anhydrite which is also expected to react during the initial period of hydration. Despite considerably lower solubility of anhydrite comparing to gypsum, anhydrite still serves in the presence of alkali solvent as a retarder of the setting forming ettringite (AFt) during the initial reactions contributing to total heat. Anhydrite in this belite rich system deserves further research since it plays an important role in terms of hydration mechanism and performance of hardened material in systems with OPC and CSA [20].

Period of slow reactions is followed by acceleration period which is characterized by the main peak related to hydration of C₃S. The position and the maximum of the peak related to C₃S hydration is changing with increasing Li content. With higher Li contents the temperature of the maximum increases and the position moves to earlier times. Total heat development during 7 days of hydration show that doping of the belite with the S and the

combination of S and Li dramatically increases the reactivity of the resulting cement (Fig. 1). The combination of S and Li accelerates the heat evolution during first days compared to doping with the S only.

C₂S hydration is very slow and heat contribution is considerably lower. C₂S reactions are represented by minute peaks in deceleration period where diffusion is the controlling process of hydration. In principle, it is claimed that both hydraulically highly active and nearly inactive forms may be possible for all belite modifications and the measured strength generation depends on the experimental conditions like burning temperature, cooling rate, foreign oxide content, etc. [21]. The reactivity of C₂S is affected by the timing of the clinker phases hydration. Since the hydration of C₂S take part mainly in deceleration period, the lack of water, space and smaller number of fine and more reactive particles are parameters affecting C₂S hydration kinetics.

3.2 Phase analysis

From results of phase composition of burned clinkers, it can be stated that the β-polymorph of dicalcium silicate content increases with doping with S and even more with combination of S and Li. Vice versa the content of γ-polymorph of dicalcium silicate decreases with the doping (Table 2). C₃S formation is significantly suppressed with increasing Li content. The reason of high amount of C₃S in C₂S S sample is related to its lower content of

unreacted residual free lime compared to lithium clinkers, and therefore the alite content is increased by the reaction of C_2S with free lime. The calculation shows that the difference from the raw meal is only about 3 wt% CaO. Given the error that the Rietveld refinement has, this difference is negligible. Recent study [22] clarifies this effect of Li by significant reduction in the temperature of the clinker melt formation and a decrease in its viscosity. Lithium causes a partial to complete decomposition of the alite into microcrystalline mixture of belite and free CaO depending on Li_2O content and cooling rate.

The phase composition was monitored by XRD hydration in situ during 24 h of hydration. Sample C_2S contains mainly γ - C_2S with a small amount of β - C_2S and a minimum of CH (CH peak is overlapped with peaks of C_2S and a slight amorphous hump). The amorphous hump is related both to C-S-H formation and water that is consumed during hydration. In the course of 24 h the phase composition does not change considerably. Sample C_2S S contains β - C_2S and γ - C_2S , C_3S and CH. Although the raw material composition was designed so that the resulting CaO: $SiO_2 + SO_3$ ratio would match belite, relatively high amount of C_3S is probably caused due to release of a part of SO_3 during synthesis. At the beginning, amorphous hump and intensity of CH peaks are increasing. From 160 min on, there is no longer a hump and CH peaks are clearly visible and their intensities increase. After 800 min., there is no change. Sample C_2S S 2Li contains β - C_2S , C_3S and CH. CH peaks appear right at the beginning and gradually increase their intensity reaching their maximum at around 360 min (Fig. 2).

β - C_2S intensities have a very slight decrease at the beginning, otherwise unchanging. C_3S intensities also decrease from the start. Sample C_2S S 4Li contains β - C_2S , C_3S , CH and anhydrite. At the beginning, a pronounced amorphous hump disappears around 200 min. From 200 min, anhydrite is visible and then its signal stays invariant. CH grows from 80 to 1200, then its intensities stay unchanged.

Detailed XRD and DTA analyses were done on sample C_2S S 2Li. Hydration of the sample was stopped after 0, 45, 90, 360, 720 and 2880 min. Phase composition including amorphous phase was determined. CaO reacts completely within first minutes of hydration, which is demonstrated as a large exothermic signal in isothermal experiments (Fig. 1). C_3S content decrease and increase of amorphous content and CH content are in good correlation with the main calorimetric peak. β - C_2S reacts very slowly showing continuous content decrease. The exact phase composition determination during first hour is problematic, because the amorphous phase includes also glassy content of the clinker and unbound water (Fig. 3).

Quantitative analysis of effluent gases with calculation of phases for single processes was done by TG/DTA/DTG on sample C_2S S 2Li (Figs. 4, 5 and 6). The phase composition of the sample was determined after 45, 90, 360, 720 and 2880 min of hydration. Position and intensity of main endotherms were monitored at selected time intervals during hydration (Fig. 3; Tables 3 and 4). Processes of H_2O release from C-S-H and AFt overlap each other. Taking in account recrystallization of AFt, continuous increase of C-S-H content can be seen on endotherm

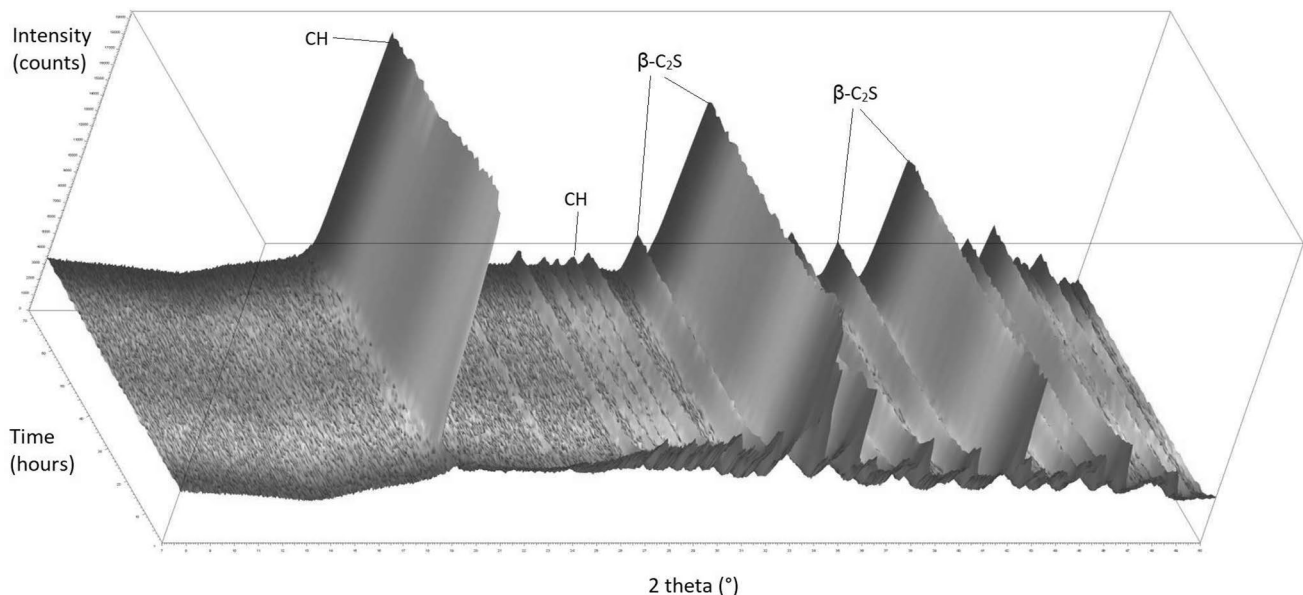


Fig. 2 XRD, hydration in situ, sample C_2S S 2Li, 24 h

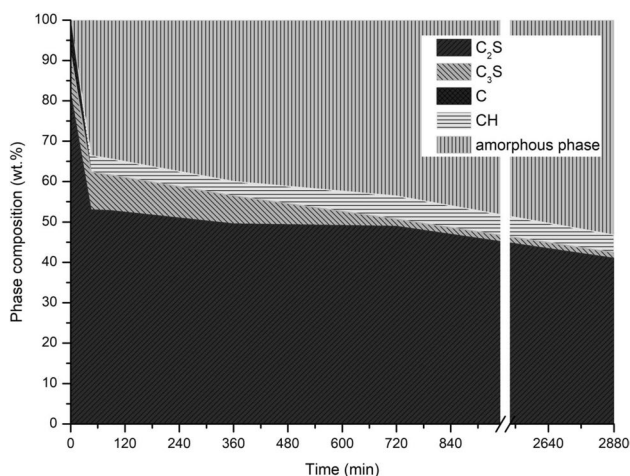
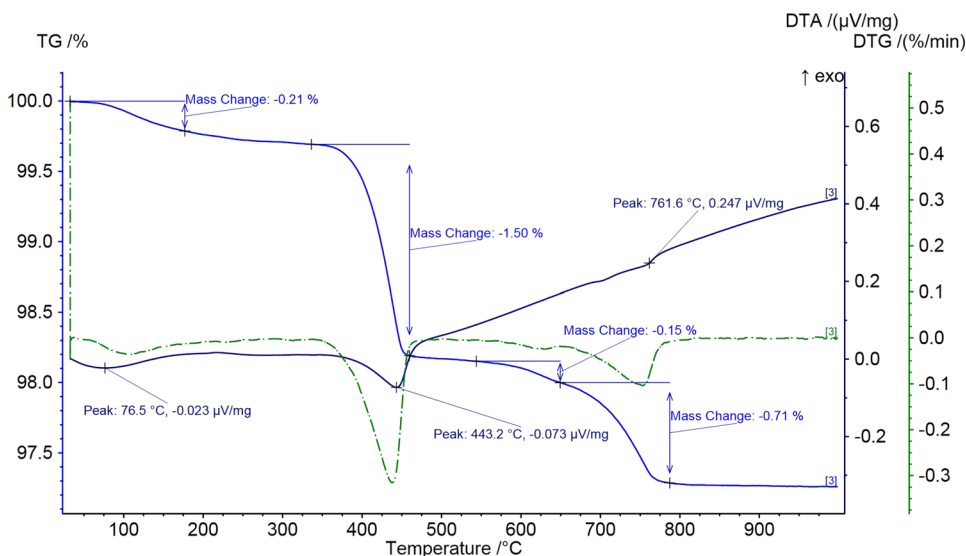


Fig. 3 XRD, inner standard method, phase composition during 2 days of hydration, sample C₂S 2Li

which changes its position from 76 to 127 °C during 48 h of hydration. CH endotherm moves its minimum as the crystal size increases. From 720 min on, double endotherm of CH is visible. This double endotherm can be explained as a second generation of CH, which might indicate the presence of another source. From the results of calorimetry and XRD, it is obvious that this source is β-C₂S which starts to react later than C₃S. Furthermore, the C₃S content stays the same after 720 min of hydration (Fig. 3). Based on the intensities and positions of endotherms, it is likely that two generations of CH differing in crystal size are formed. Second generation, that is detectable from about 6 h of hydration onwards, grows simultaneously with first generation.

Fig. 4 TG/DTA/DTG, 45 min of hydration, sample C₂S 2Li



3.3 Microstructure

Development of the structure during hydration of C₂S 2Li cement paste was observed by SEM in secondary electrons. The microstructure after 45 min, 90 min, 360 min, 720 min and 2880 min is given in Fig. 7. A study [23] that has discussed the microstructure of a similar system after 90 and 180 days of hydration revealed similar C–S–H fibrous structures, that was transformed into dense aggregates of globular morphology at later ages (180 days).

The studied structure shows platy larger CH crystals with undergrowth of fine fibrous C–S–H after 45 min and 90 min of hydration and continuous recrystallization of CH and densification of C–S–H on the surface of the particles after 2880 min of hydration. Based on SEM-SE, it is not possible to distinguish C–S–H formed from C₃S and C₂S hydration, yet it is the goal of further microstructural studies. Nevertheless, the densification of C–S–H from 720 min on, taking into account the phase analyses, can be supported by C₂S hydration.

4 Conclusions

Correlation of doping and resulting reactivity of clinker and cement is problematic due to the fact that doping will change the distribution of clinker phases and thus several parameters at the same time. Due to doping with S, the β-C₂S content increased and this was even more pronounced in the case of doping with the combination of S and Li. Undoped C₂S sample with high content of γ-C₂S is significantly less reactive compared to doped samples. The main exothermic peak related to C₃S hydration and C–S–H formation is changing with increasing Li

Fig. 5 TG/DTA/DTG, 720 min of hydration, sample C₂S S 2Li

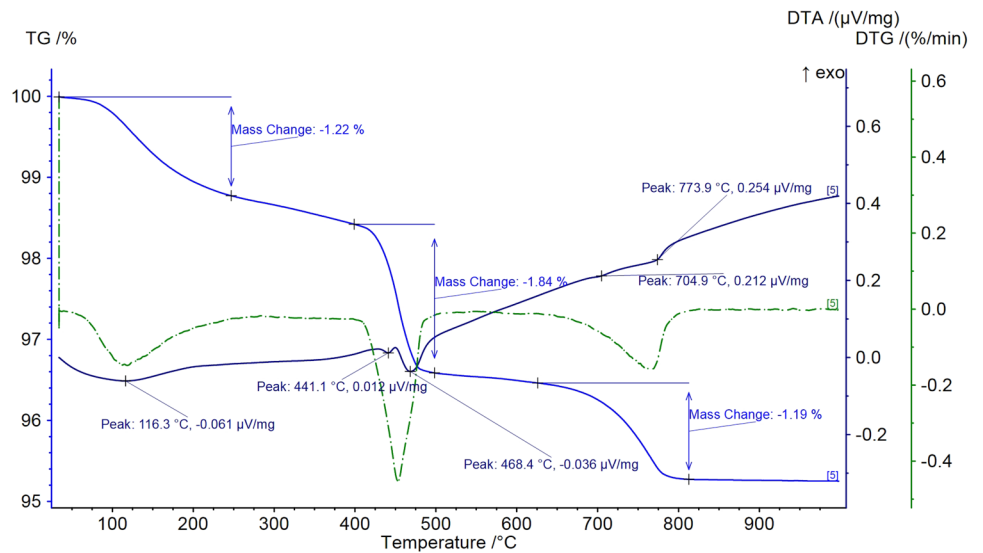


Fig. 6 TG/DTA/DTG, 2880 min of hydration, sample C₂S S 2Li

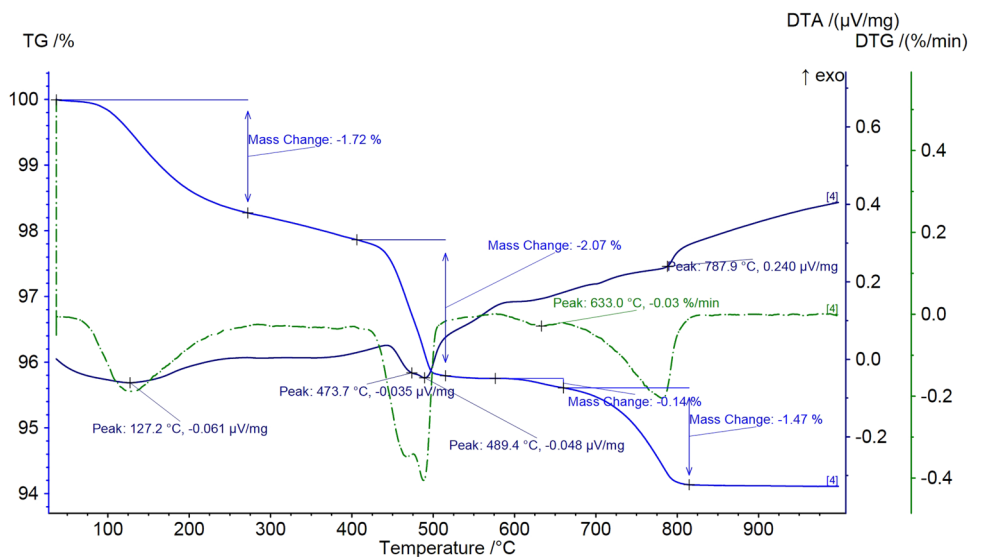


Table 3 Quantification of effluent gases or phases* from thermographs (wt%), sample C₂S S 2Li

	45 min	90 min	360 min	720 min	2880 min
H ₂ O; C–S–H, AFt	0.21	0.18	0.47	1.22	1.72
H ₂ O; CH	1.5	1.56	1.36	1.84	2.07
CH*	6.17	6.42	5.59	7.57	8.51
CO ₂ ; calcite* (minor peak)	0.15	0.16	0.4	–	0.14
CO ₂ ; calcite* (larger peak)	0.71	0.41	1.07	1.19	1.47
CO ₂ ; calcite* (sum)	0.86	0.57	1.47	1.19	1.61
Calcite*	1.96	1.30	3.34	2.71	3.66

Table 4 Position of endotherms (°C), sample C₂S S 2Li

	45 min	90 min	360 min	720 min	2880 min
C–S–H, AFt	76	96	99	116	127
CH	443	441	451	441, 468	474, 489
Calcite (main peak)	762	739	777	774	788

content. Its position moves to earlier times and its intensity increases. The reactivity of β-C₂S is affected by the timing of the hydration of other clinker phases. Based on heat development, the formation of C–S–H products is a continuous process that relates mainly to C₃S hydration during first 6 h which is then supported also by slow reaction of β-C₂S. Results of thermal analyses

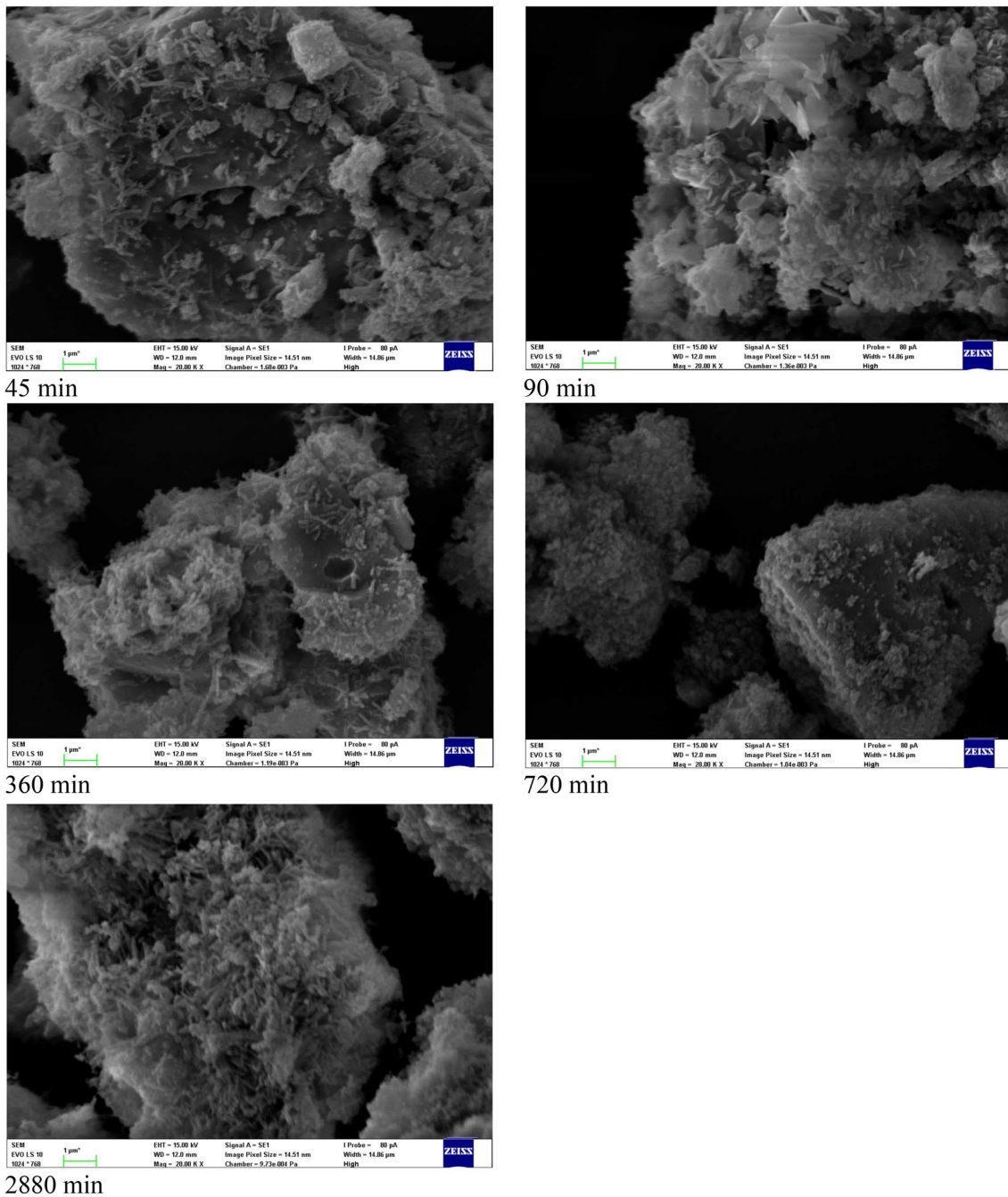


Fig. 7 SEM micrographs of sample C₂S 2Li during 48 h of hydration, 20,000x

show the presence of double portlandite endotherm in DTA curves revealing two generations of portlandite attributed to C₃S and C₂S hydration. This finding is in agreement with changes in phase composition and position of exotherms determined by XRD-in situ and inner standard method, isothermal calorimetry and densification of C–S–H on the surface of the anhydrous particles studied by SEM.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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