COMBINED EFFECT OF LI, CU AND S DOPING ON STRUCTURE AND HYDRATION OF β-DICALCIUM SILICATE

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Abstract

This study investigates the effect of Li, Cu and S on the structure and hydration of the beta modification of dicalcium silicate (β-C_2S). The doped β-C_2S phase was prepared by burning beta-C_2S with dopant sources. The structure of prepared β-C_2S samples was examined using X-ray diffraction, scanning electron microscopy and infrared spectroscopy. Heat evolution during hydration was assessed by isothermal calorimetry. A positive effect on cement hydration was observed for several dopant combinations.

Keywords

Dicalcium silicate, clinker phase doping, hydration, isothermal calorimetry, X-ray diffraction

1 INTRODUCTION

Cement production continues to grow and reached 4.4 billion tonnes worldwide in 2021 and is responsible for roughly 7% of global CO_2 emissions. Roughly 50% of CO_2 emissions are related to limestone calcination and 40% to energy consumption during the burning process [1]. Several strategies have been suggested and are being implemented, in order to reduce the carbon footprint of cement production. Most significant of those are the use of supplementary cementitious materials in order to lower the total clinker content in cement, and alternative clinker compositions. One of the alternatives to ordinary Portland cement (OPC) are reactive belite-rich Portland clinkers (RBPC). These clinkers have a similar mineralogical composition to OPC, with belite being the most abundant phase [2]. As dicalcium silicate (C_2S) is the main clinker phase, the lime saturation factor of the raw feed can also be reduced, thereby reducing the CO_2 released during limestone calcination [3]. The typical burning temperature for RBPC is also about 100°C lower than for OPC, effectively lowering the energy consumption related to the burning process [2].

Due to the lower hydration rate of belite-rich cements in the early stages of hydration, in addition to rapid cooling, activation by suitable dopants is typically used during the production of RBPC [4]. The main purpose of these constituents is twofold. The first reason is to add fluxes, which reduce the temperature at which the liquid phase forms, or mineralizers, which change the viscosity and surface tension of the melt. Both of those effects can increase the energy efficiency of the burning process. The second reason to add dopants is to increase the hydraulic activity of RBPC by either stabilization of more active polymorphs or distorting their structure leading to higher reactivity.

Combination of Li, Cu and S as dopants in RBPC has already been investigated and shown to be promising due to the combined effects of these elements. Sulfur promotes the stabilization of β-C_2S with a large unit cell volume, while a combination with alkaline oxides can lead to the stabilization of α'$_H$-C_2S [5]. Cu acts as a flux and lowers the melt formation temperature and promotes grain growth [6]. Cu also typically has a positive effect on the long-term strength of concrete, but can severely inhibit hydration in the early stages [7]. Computational studies by Hou et al., however, suggests that Cu doping could increase reactivity and hydration rate of β-C_2S [8]. Increasing the Li content in cement, on the other hand, increases the early hydration rates, negating the slow development of early strength, which is the main drawback of RBPC [9].

The focus of this study is to investigate the combined effect of Li, Cu and S on the hydration and structure of β-C_2S. Due to the complexity of the cement hydration process, understanding the influence of dopants on individual clinker phases, is of crucial importance in order to assess their role in real cement systems. Their

influence on C_2S is especially important for low-energy cements, since it is the most abundant phase in typical belite-rich cements.

2 METHODOLOGY

β-C_2S of 100% purity was stabilized with 0.8 wt.% BO_3 and was prepared by high-temperature synthesis at a temperature of 1400 °C. Reagent-grade Li_2CO_3, $(NH_4)_2SO_4$, and CuO were used as dopant sources. Selected dopant levels were calculated as oxide equivalents at 0.2 and 1 wt.% for CuO and Li_2O, and 0.5 and 2 wt.% for SO_3. The mixture of β-C_2S with dopant sources was homogenized by milling in a vibrational mill. Green body pellets with diameter of 4 cmwere prepared using a laboratory hydraulic press. The pellets were then burned on a platinum plate in an air atmosphere at 1450 °C with a holding time of1 hour. Compositions of green-body pellets for selected dopant combinations are given in Tab. 1.

Tab. 1 Raw meal compositions used for the preparation of doped β-C2S.

Sample number	Sample	CuO	Li_2CO_3	$(NH_4)_2SO_4$	β-C_2S
1	β-C_2S 0	0	0	0	40
2	β-C_2S 0.2CuO-0.2Li_2O-0.5SO_3	0.080	0.196	0.330	40
3	β-C_2S 0.2CuO-0.2Li_2O-2SO_3	0.080	0.196	1.320	40
4	β-C_2S 0.2CuO-1Li_2O-0.5SO_3	0.080	0.988	0.330	40
5	β-C_2S 0.2CuO-1Li_2O-2SO_3	0.080	0.988	1.320	40
6	β-C_2S 1CuO-0.2Li_2O-0.5SO_3	0.400	0.196	0.330	40
7	β-C_2S 1CuO-0.2Li_2O-2SO_3	0.400	0.196	1.320	40
8	β-C_2S 1CuO-1Li_2O-0.5SO_3	0.400	0.988	0.330	40
9	β-C_2S 1CuO-1Li_2O-2SO_3	0.400	0.988	1.320	40

X-Ray diffraction (XRD) analysis of the phase composition of prepared samples was carried out on a D8 Advance diffractometer (Bruker) with a Cu anode ($\lambda_{K\alpha}$ = 1.54184 Å) and Bragg-Brentano parafocusing geometry.

Structural changes of β-C_2S were studied by attenuated total reflection infrared spectroscopy (ATR-FTIR) using a VERTEX 80 vacuum FTIR spectrometer (Bruker optics). All measurements were carried out in a vacuum in the wavenumber range of 525-4000 cm^{-1} with a resolution of 2 cm^{-1}. Each measured spectrum is an average of 64 scans. The background spectrum was measured before each measurement and the signal was subtracted. All infrared spectra have been normalized for better clarity.

Maps of element distributions were obtained via a scanning electron microscope Zeiss EVO LS10 with energy dispersive X-ray analyser X-max 80 mm^2 (Oxford Instruments).

β-C_2S hydration was investigated using an 8-channel isothermal calorimeter TAM air (TA Instruments). Samples were ground for 2 minutes in a vibrational mill. The measured samples consisted of 7 g of C_2S and 3.5 g of water. Water with the same thermal capacity was used as a reference and results were normalized for 1 g of dry sample. All equipment, samples and mixing water were tempered to 25°C prior to mixing. Samples were mixed externally and measurements were carried out at 25°C for 830 hours.

3 RESULTS

Tab. 2 Phase composition of prepared β-C2S samples.

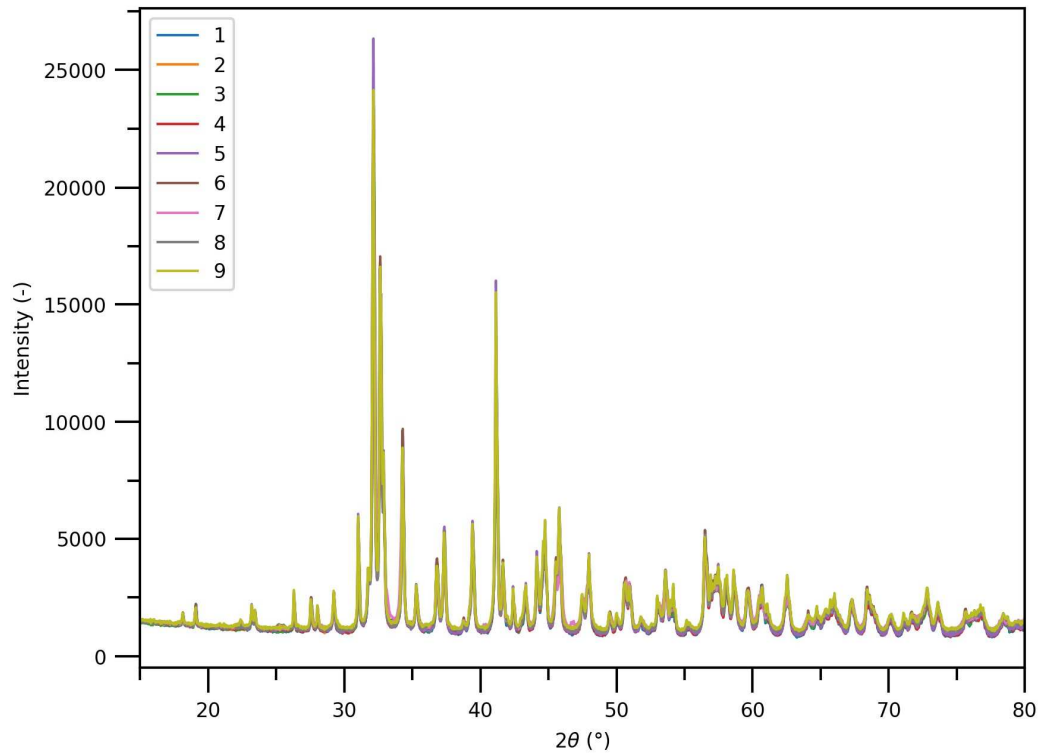| Sample	1	2	3	4	5	6	7	8	9
β-C_2S	99.8	99.6	99.7	98.5	99.4	99.6	96.7	98.6	99.1
α'_H-C_2S	-	-	-	-	-	-	3	-	-
Quartz	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.1	0.3
Anhydrite	-	-	-	1.0	-	-	-	0.9	0.3
Li_2SO_4	-	-	-	-	0.2	-	-	-	0.1
Cuprite	-	0.1	0.1	0.3	0.2	0.2	0.1	0.4	0.2

Fig. 1 X-ray diffractograms of doped β-C₂S.
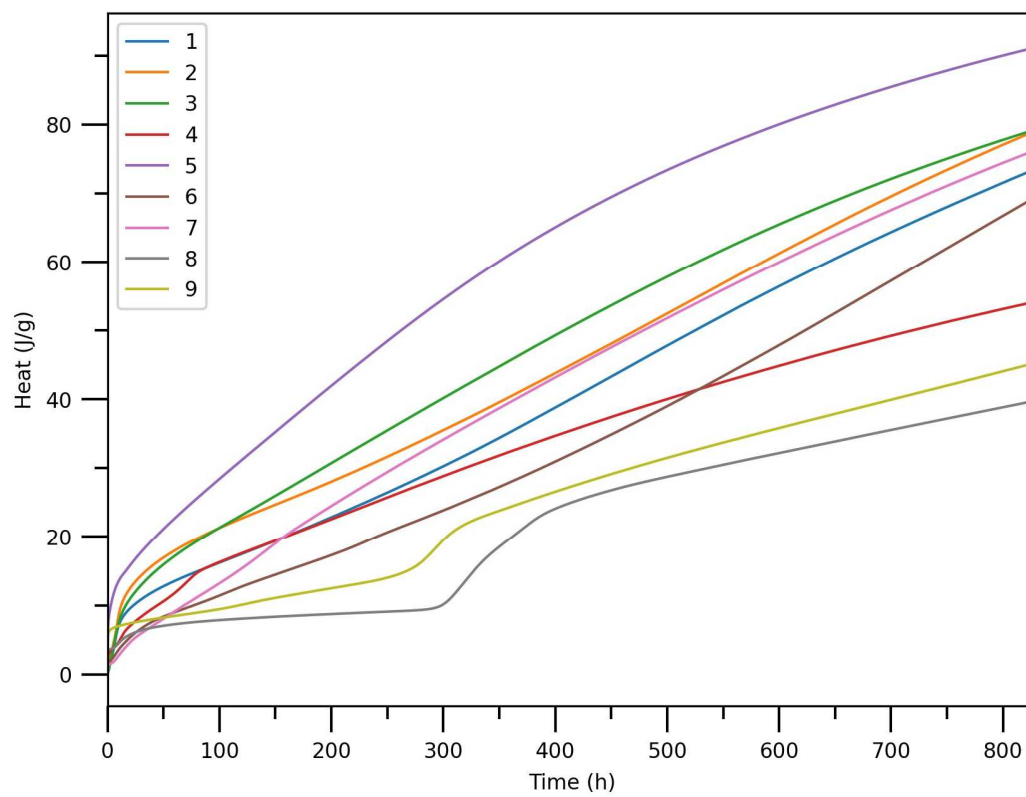

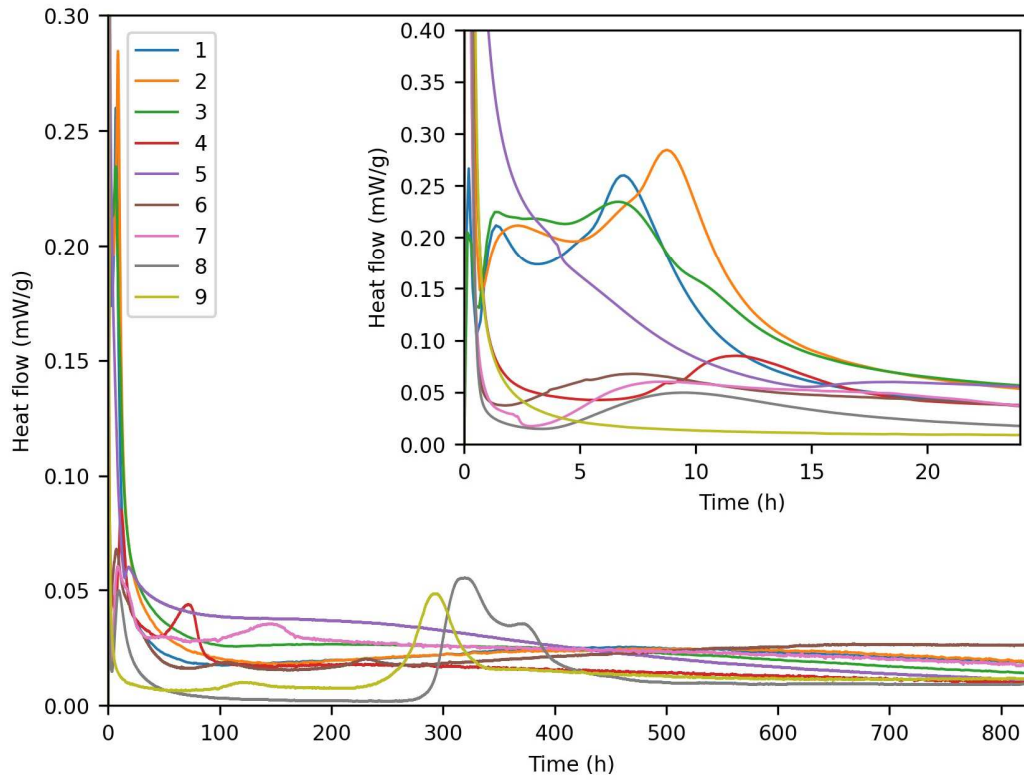Fig. 2 Total evolved heat during 830 hours of hydration of β-C₂S at 25°C.

Fig. 3 Heat flow during the first 830 hours of hydration of β-C_2S at 25°C.
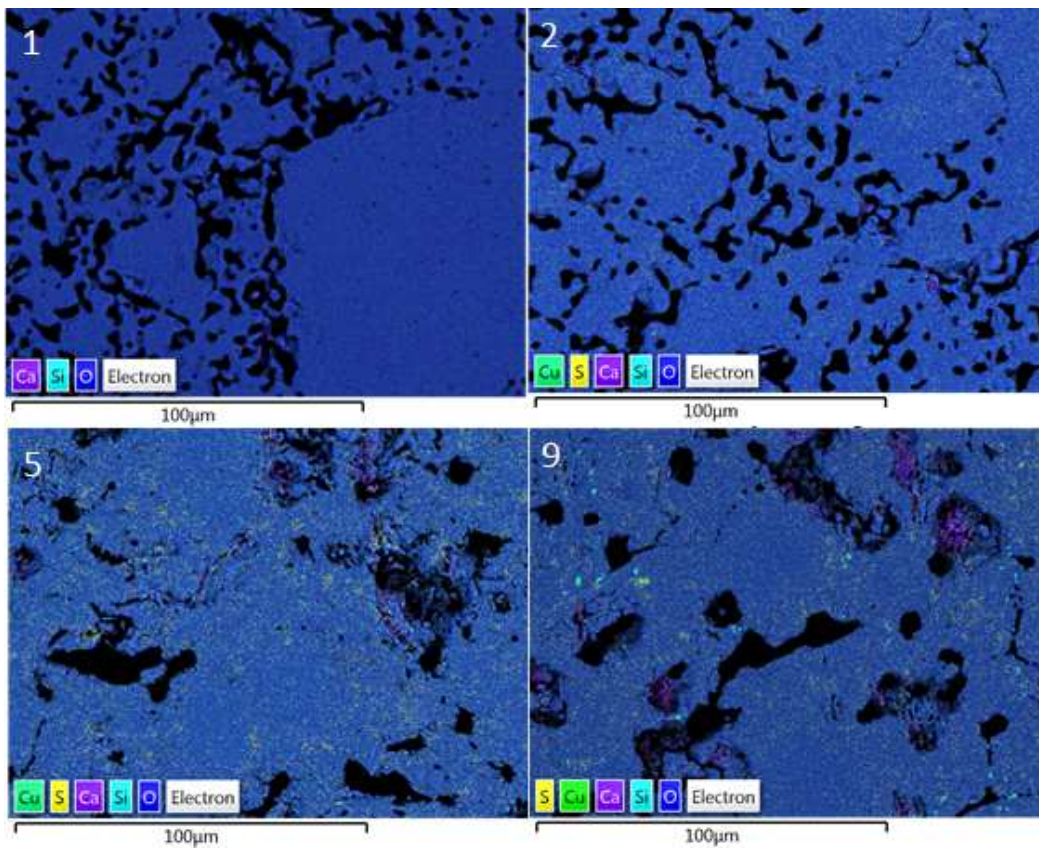

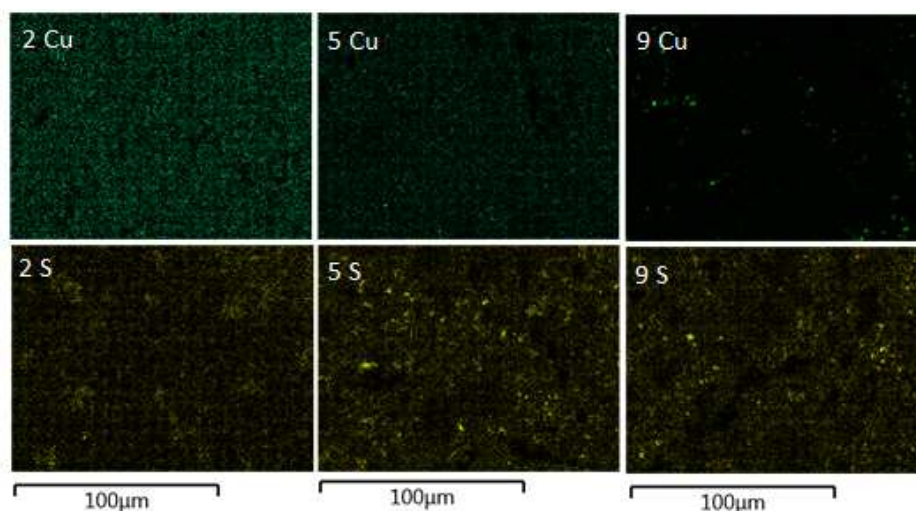Fig. 4 SEM-EDS maps of selected samples at 2000× magnification.

Fig. 5 Distribution of S and Cu in selected samples. SEM-EDS maps at 2000× magnification.
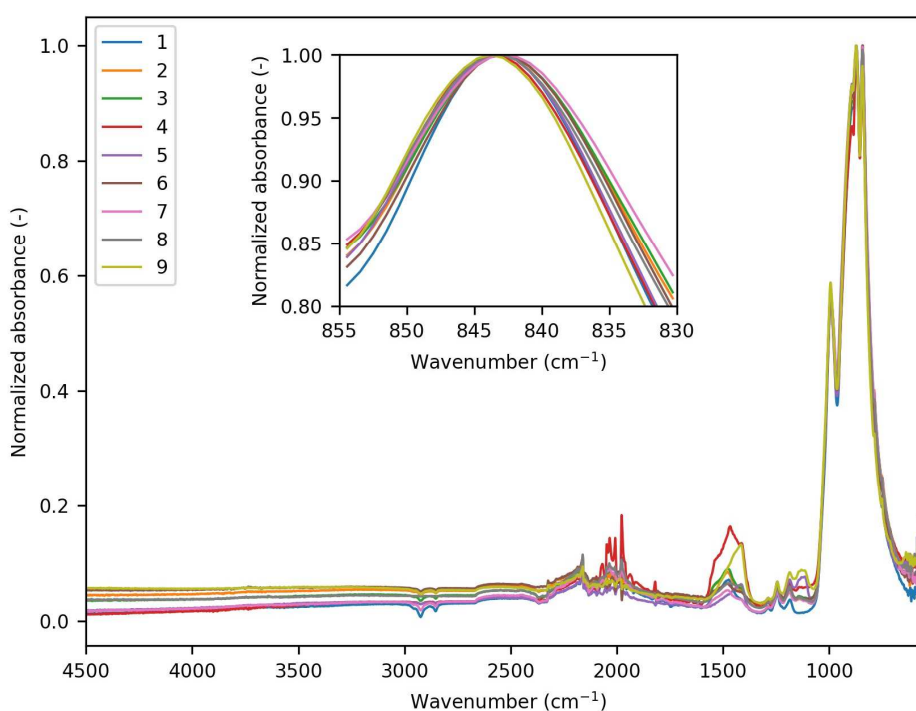

Fig. 6 Infrared spectra of doped β-C_2S.

4 DISCUSSION

The phase composition of prepared samples and their XRD spectra can be seen in Tab. 1 and Fig. 1., respectively. β-C_2S was found to be the only clinker phase in prepared samples and no undesirable transformation to the γ-C_2S modification was observed during sample preparation. An exception to this was sample 7, where a small amount of C_2S underwent transformation to the α'$_H$-C_2S modification. A small amount of quartz was detected in all samples regardless of the dopant presence. Its origin is likely a minor contamination during sample preparation. In samples 4, 8 and 9 present sulfur caused anhydrite formation. Anhydrite formation in SO_3-activated clinkers seems to be promoted by the increased Li content and was only observed in samples containing 1 wt. % Li_2O. In the samples doped with a high amount of SO_3 and Li, a small amount of $LiSO_4$ was also formed. All doped samples contained a minor amount of cuprite. Generally, a higher amount of Li seems to cause the formation of additional phases during the preparation process of doped β-C_2S.

The influence of the dopants on the hydration of β-C$_2$S was studied by isothermal calorimetry. The total evolved heat during hydration is shown in Fig. 2. An increase in the total evolved hydration heat, compared to the reference β-C$_2$S, was achieved with dopant combinations 2, 3, 7 and 5. A high amount of Cu caused significant retardation of β-C$_2$S, resulting in lower hydration heat evolved, especially in the early stages. This observed effect is in agreement with the literature [7]. In sample 7 doped with 2 wt. % of SO$_3$, this effect was offset and the degree of hydration was higher than the reference sample after 150 hours. The desired effect was achieved with sample 5, where hydration heat exceeded the reference in both the early and late stages of hydration, corresponding to a 64% increase after 24 hours and 24% after 830 hours. Samples 2 and 6 also showed promising results in terms of the potential effect on long-term strength as an increasing trend can be observed in the hydration curves. This is consistent with the effect of Cu on the long-term hydration of β-C$_2$S [7]. With the 1 wt. % CuO content in sample 6, the negative effect on early hydration resulted in worse performance compared to the reference sample.

The heat flow during hydration is depicted in Fig. 3. The initial 24 hours of hydration are shown in the inset of Fig. 3. The double peak associated with the intensive heat evolution of the initial hydration can be seen. The position and intensity of this double peak remained relatively similar to the reference for samples 2 and 3, which also showed similar behaviour with increased total hydration heat throughout the hydration process. Cu doping, however, significantly increased the induction period [8]. This effect was most severe in samples 8 and 9, where the induction period was more than 200 hours, making these compositions effectively unusable in conventional cement applications. In sample 5, high levels of Li and SO$_3$ altered the hydration behaviour significantly [9]. The induction period and the double peak were not observable. The stage of the initial hydration then continued directly into the main hydration peak of β-C$_2$S, causing higher heat flow compared to the rest of the prepared samples. The deceleration stage of hydration is achieved only after 200 hours of hydration, which roughly corresponds to the onset of the main hydration peak of the reference sample. It is important to note, that although the initial hydration peaks show higher heat flow values, the second hydration peak contributes significantly more to the total heat of hydration, which is relevant to the long-term properties of belite-rich cements as C$_2$S is a significant contributor to the long-term strength of the final cement composites [2].

Elemental maps for selected samples are shown in Fig. 4. Samples 1, 2, 5 and 9 were selected based on their composition and isothermal calorimetry results. In Sample 2 containing 0.2 wt. % of CuO and 0.5 wt. % SO$_3$, a homogeneous distribution of dopants was observed. Increasing the SO$_3$ content to 2 wt. % resulted in inhomogeneities in the sulfur distribution in sample 5. However, this inhomogeneity did not have a significant negative effect on the hydration as described earlier in isothermal calorimetry results. The appearance of sulfur-rich areas also did not seem to cause changes in the Cu distribution in the sample. In contrast, sample 9 containing 1 wt. % CuO and 2 wt. % SO$_3$ had both areas with increased Cu and S content. Cu in this sample appears to be concentrated in small regions compared to the homogeneous distribution in previously mentioned samples. This is consistent with the earlier finding that Cu is incorporated in the clinker phases only in limited amounts and preferably forms a secondary cuprite phase (Cu$_2$O) or a double oxide CaO.2CuO [10]. Formed anhydrite particles in sample 9 can also be identified from the Si-depleted regions.

FTIR spectra of prepared β-C$_2$S are shown in Fig. 6. Typical β-C$_2$S vibrational bands are located at 845 cm^{-1} for v_s Si–O symmetric stretching of the Si-O bond and 995 for v_{as} Si–O asymmetric stretching [11]. A small shift in the v_s Si–O band to higher wavenumbers can be seen for samples containing 1 wt. % Li, indicating a distortion of the β-C$_2$S structure. A small band at 787 cm-1 can be assigned to quartz Si-O stretching vibration [12]. Vibrational bands related to the presence of sulfate can be seen at 1115 [13] cm^{-1} and 1185 cm^{-1} [14].

5 CONCLUSION

β-C$_2$S with 8 combinations of Li, Cu and SO$_3$ dopant concentrations were prepared and the influence of dopants on the structure and hydration processes was investigated. A small amount of secondary phases was formed during preparation. A high content of Li in the sample lowered the solubility of SO$_3$ in β-C$_2$S and caused formation of anhydrite. Higher doping with S, in turn, caused the formation of LiSO$_4$ in samples containing 1 wt. % Li. Cuprite formed in all samples because Cu enters the clinker phases only to a limited extent.

The distribution of elements studied by SEM-EDS showed that for both Cu and S, lower doping levels allowed their homogeneous distribution throughout the β-C$_2$S phase. At higher doping levels, an inhomogeneous distribution was observed for both Cu and S. However, a negative effect on the hydration process was only observed for the former. The structure of doped β-C$_2$S was also studied by FTIR. A small shift was observed for the v_s Si–O band in samples with high Li content, possibly indicating a distortion of the β-C$_2$S structure.

The hydration process was studied by isothermal calorimetry for 830 hours. Several samples resulted in an increase in the total heat of hydration evolved. Cu doping significantly slowed down the hydration, with 1 wt. % Cu extending the induction period to several hundred hours in some cases. The best results were achieved with 0.2 wt. % Cu, 1 wt. % Li and 2 wt. % SO$_3$ doping. With this combination, the hydration behaviour of β-C$_2$S

was altered significantly and the induction period was not observed on the calorimetric curve and the deceleration period was reached only after 200 hours of hydration.

Acknowledgement

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