

Antagonistic effect of superplasticizer and colloidal nano-silica in the hydration of Alite and Belite pastes

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Abstract The dependence on the hydration rate for Alite and Belite clinker phases in the presence of a polycarboxylate superplasticizer PC SP upon addition of colloidal nano-silica CNS were monitored by means of Diffuse Reflectance Infrared spectroscopy DR-FTIR. Spectral signatures of clinker dissolution and product formation were acquired for both materials. The rates for the build-up of product vibrational band intensities were found to depend sensitively on addition of CNS. The hydration product was proposed to be calcium-silicate-hydrate C-S-H. Details in the spectral signatures were found to differ. Quantum chemical calculations were employed and found to be consistent with the interpretation that small clusters dominate the Alite C-S-H spectrum, whereas the Belite C-S-H spectrum results from extended polymers.

Introduction

The hardening process of Portland cement involves two time scales, reflecting those of the two dominant components, Alite and Belite. In case of Alite, the time

scale is that of hours up to weeks, whereas Belite hydration time is known to range from weeks to years. A long-standing issue in cement development concerns the activation of Belite so that an effective continuous hardening process is achieved. An additional incentive for finding such an accelerator is the reduced environmental impact and the improved economy that would follow an increase in the Belite/Alite ratio in commercial cements.

Superplasticizers SP's are surface-active agents which modify interparticle forces between cement particles and thus make them disperse. Entrapped water is thereby released, and in so doing the flowability of the cement paste is increased. SP's belong to different basic groups such as: lignosulfonates, melamines, naphthalenes and polycarboxylates PC. The PC based polymers have long polyethylene oxide side-chains containing carboxylic functional groups grafted onto its backbone. Polymer optimization may concern backbone length and the amount of grafted side-chains. The additions of SPs decrease the rates of hydration product formation during cement clinker hydration [1–5].

Colloidal Nano-Silica CNS denotes small particles consisting of an amorphous SiO₂ core with a hydroxylated surface, which are insoluble in a stabilizing electrolyte solution in order to ensure a prolonged shelf time (~1 year). The size of the particles can be varied between 1 and 500 nm, hence they are small enough to remain suspended in the water medium. Increasing the ion strength in the electrolyte induces gel formation, whereby the CNS particles agglomerate [6]. Parameters such as specific surface area, size and size distribution can be controlled by the synthesis technique. The nano-meter sized particles display a

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high specific surface area, and thus they constitute a highly reactive siliceous material in the context of cement chemistry.

Comprehensive investigations on the influences of CNS during the hydration process of Belite and Alite clinker phases have previously been undertaken [Björnström and Panas, Submitted]. These involve detailed investigations of each constituent, and a central finding is the accelerated saturation of Diffuse Reflectance Fourier Transform InfraRed DR-FTIR spectral intensities with time when CNS is present. It was demonstrated that the nano-silica particles do not dissolve in Alite or Belite matrices, rather they were interpreted as Ca^{2+} and SiO_4^{4-} sinks. As the time scale for pure Belite hydration is that of weeks up to years it was possible to resolve information regarding the different stages of the hydration process [Björnström and Panas, Submitted]. The initial hydration of Belite was understood in terms of a three-stage process, i.e. an initial 2–3 weeks dormant stage followed by an initial dissolution stage, which preceded the long-term continuous hydration stage. During the initial dissolution stage, calcium-silicate-hydrate C–S–H was the dominant product. The long-term hydration stage, was characterised by water consumption during Belite dissolution, and water recovery upon precipitation of C–S–H and amorphous silica. The addition of 5% CNS resulted in a Belite hydration process in which the two initial stages apparently disappeared. And the continuous stage was entered already after 24 h of hydration. Quantum chemistry was employed to demonstrate consistency in such an interpretation. A C–S–H model compound was formulated and shown to produce a quantum chemically computed vibration spectrum, which maps well that of the DR-FTIR experiments. A scenario was outlined for the hydration process.

The short-term quality of a real mortar depends on parameters such as workability, setting time, and time scale of strength development. In order to achieve a cost effective such product in a rational way, it is necessary to determine how additives interfere in the mortar during hydration. The purpose of this work becomes to demonstrate the antagonistic effects of the SP retardant and the CNS accelerator in the hydration of cement. This is done here by studying the hydration of each of the clinker components separately exposed to SP and CNS by means of DR-FTIR. Because the two clinker components display different time scales for hydration, study of the fast Alite/SP/CNS system may produce a fine tuned early strength cement. In case of the slower Belite component, workability is not a crucial issue but rather the reduction of the initial dormant stage. As CNS was demonstrated to effec-

tively remove this phase, it becomes important to determine the effect of SP on the CNS activation of Belite hydration.

Experimental

Pure monoclinic β - C_2S Belite and pure triclinic C_3S Alite were supplied by Construction Technology Laboratories (Skokie, Illinois, USA). The colloidal nano-silica sol used (Cembinder[®] 50) contained 15-wt% of solid material. The particle size was 5 nm with a $500 \text{ m}^2/\text{g}$ specific surface area, supplied by EKA Chemicals AB, Bohus, Sweden. A polycarboxylate-based superplasticizer in a solution containing 30–33% active material was supplied by Sika Sverige AB, Sweden. The clinker pastes under investigation were hydrated in sealed containers, stored under humid conditions, prior DR-FTIR measurements. The water demand to achieve a homogeneous and workable paste is different between the two clinker phases. This is owing to their very different rates of hydration. Thus, C_2S pastes were mixed with a water-to- C_2S ratio of 0.35, and the C_3S pastes were prepared with a water-to- C_3S ratio of 0.30. The dosage of SP were 1 wt% of the solution, with respect to the weight of the clinker phase, the SP added was diluted in the mixing water. Where CNS was present it was also diluted in the mixing water here to ensure a homogeneous particle distribution. The dosage of CNS used were 5 wt% of the *sol*, with respect to the weight of clinker phase.

All spectroscopic measurements were carried out in a diffuse reflectance (DR) mode. The typical probe area in the present DR-FTIR experiments had a diameter of 5–7 mm, and the observed spectra, therefore, provide information about the state of the sample surface on a macroscopic scale. It is also important to stress that no direct mechanical influence on a sample surface (e.g. scraping or pressing with covering windows) was performed during the measuring procedure. This warrants that the obtained spectra reflect only the changes due to the hydration process. Spectra were recorded with a Nicolet Magna-IR 560 E.S.P. spectrometer, with a sample compartment under constant dry-air (*g*) flow, equipped with a standard diffuse reflectance unit (Graseby Specac). The spectral resolution was set to 4 cm^{-1} and all spectra were collected as an average over 64 scans. The clinker pastes were cast in the DR-FTIR sample holder and covered with Para Film[™] during hydration to prevent evaporation of water, i.e. make the curing conditions as homogeneous as possible, and to obtain smooth sample

surfaces. After achieving desired hydration times the covering film was removed and the samples were allowed to dry for 7 h under the flow of dry air in the sample compartment, stopping the dissolution process by forcing residual water to evaporate. This procedure was validated in [7].

The computational procedure for the quantum chemical calculations employed the DMOL³ program package [8, 9] as implemented in MATERIAL STUDIO (Distributed by Accelrys inc.). The BLYP density functional [10, 11] was used throughout. The double numerical basis set with a polarization function on all but the H atoms DND, and that including a p-function on H were compared and were found to display negligible differences in the spectral range of interest in the present study. Thus, only results for the DND set are presented. Vibrational frequencies were computed from numerical Hessians, and validation of possible stationary states on the potential energy surfaces were made by checking for any imaginary frequencies.

Representation of the clinker morphology was produced by means of a LEO ULTRA 55 scanning electron microscope in low-vacuum mode in conjunction with a field emission gun set at 10 kV accelerating voltage.

Results and discussion

Results from previous studies [Björnström and Panas, Submitted] imply that CNS particles do not dissolve in spite of the high alkalinity in the mortar. This is because of the monomeric silica activity, resulting from the very clinker dissolution process responsible for the alkalinity. Significant acceleration of the initial hydration rate of Belite paste was observed upon addition of CNS. DR-FTIR spectroscopy and quantum chemistry suggest the rapid C–S–H formation on the active CNS surface to be the cause of the acceleration effect.

The present study concerns the influence of PC SP on the CNS accelerator during the early hydration of the C₃S (Ca₃SiO₅, Alite) and C₂S (Ca₂SiO₄, Belite) clinkers. Thus, the complexity of our model mortar is increased to include the PC SP to the clinker/CNS/C–S–H system. Sample preparation and procedure for analyzing spectra, developed in the former works, are the same as in [Björnström and Panas, Submitted].

In what follows, C–S–H absorption signatures in the interval 800–1300 cm⁻¹ are reported, implying wavelengths in the range 7–12.5 μm. Thus, hydration characteristics are monitored a few tens of micrometers into the mortar (compare Fig. 1). The degree to which this sampling procedure is representative of the mortar

bulk was subject to investigation in [7]. The rate of product formation as measured by differential scanning calorimetry, which is a bulk technique, was found to correlate with the rate of clinker dissolution observed by DR-FTIR.

Initial hydration of Alite/SP

The time evolution of the Alite hydration spectrum for samples which include 1% SP is displayed in Fig. 2. Here the characteristics of the hydration process are monitored by examining the DR-FTIR spectra for increasing hydration times after subtracting the corresponding 4 h spectra. The first signatures related to Alite activity were acquired after 12 h of hydration. This is consistent with the understanding that SP:s act

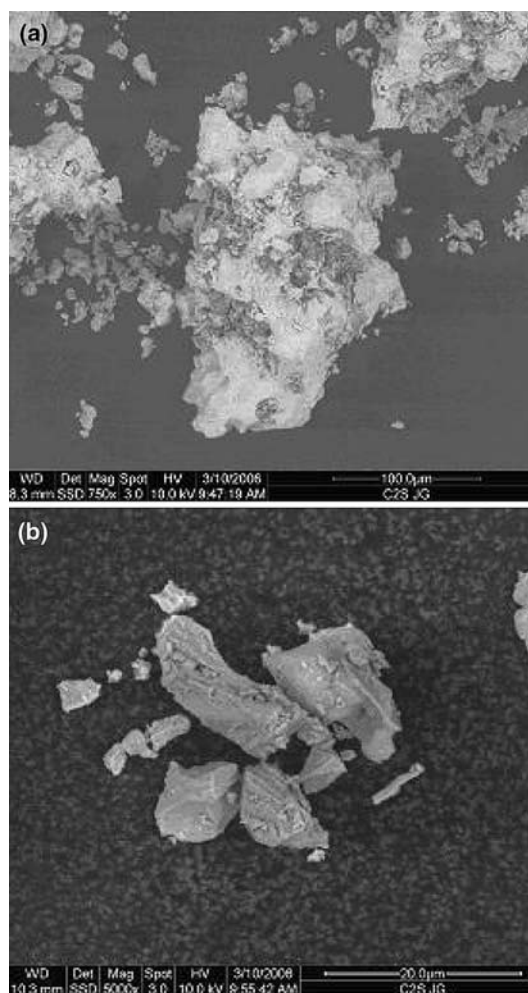


Fig. 1 Representation of the clinker morphology produced by means of SEM in a low vacuum mode. Here, (a) represents the fractured surface of a large Belite particle (~100 μm) and (b) emphasizes the range of particle sizes in the sample, down to ~1 μm

as hydration retardant. What was interpreted as a signature of Alite dissolution in [7], i.e. loss of IR intensity in the $650\text{--}900\text{ cm}^{-1}$ interval, is seen again in Fig. 2. The spectral feature in the $900\text{--}1050\text{ cm}^{-1}$ interval has not been seen before in case of Alite. This product signature was associated with calcium-silicate-hydrate C-S-H formation in the Belite study [Björnström and Panas, Submitted]. Interestingly, the build-up of this band is preceded during the first 24 hours by an initial band some 50 cm^{-1} higher in frequency. Also, the C-S-H signature grows on the expense of the background at $1000\text{--}1200\text{ cm}^{-1}$. Apparently, the decomposition of the former is accompanied by the latter. Both these processes are understood to result from dissolution phenomena. The transient peak is taken to signify initial phase separation of $\text{Ca}(\text{OH})_2$ during build-up of SiO_2 oligomers, which subsequently react to form C-S-H. Given that DR-FTIR is a surface sensitive technique, the fact that the background at $1000\text{--}1200\text{ cm}^{-1}$ experiences loss of intensity simultaneously with the formation of C-S-H may be taken to suggest the presence of SiO_2 oligomers also in the surface of the clinker particles. Saturation of the C-S-H spectral signature is achieved after 48 h.

Initial hydration of Alite/SP/CNS

The product evolution upon mixing Alite with SP and CNS is similar to that of the Alite/SP, as seen in Fig. 3. What comes out different is the time scale alone. Thus, spectral saturation is achieved already after 24 h, and reformation of transient products and clinker phase specific surface species is seen to have started to take place already after 4–12 h of hydration.

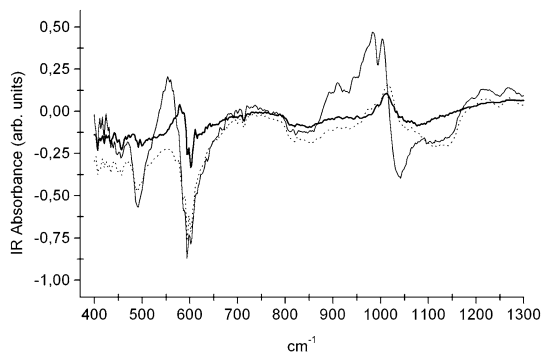


Fig. 2 DR-FTIR spectra of superplasticized Alite hydrated for 12 h (bold line), 24 h (dotted line) and 48 h (solid line) after subtracting the spectrum of a 4 h hydrated superplasticized Alite sample

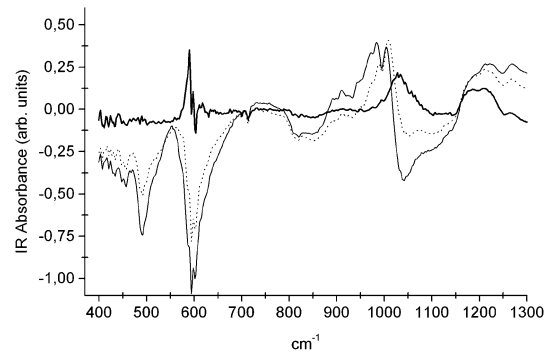


Fig. 3 DR-FTIR spectra of superplasticized Alite containing 5% CNS hydrated for 4 h (Bold line), 12 h (dotted line) and 24 h (solid line) after subtracting the spectrum of a 4 h hydrated superplasticized Alite sample

Initial hydration of Belite/SP

Belite is the slow clinker component of Portland cement. A measure of this well-known behaviour, employing DR-FTIR, was obtained in a previous study [Björnström and Panas, Submitted]. In that study, C-S-H product formation commences only after some 3 weeks and spectral saturation was achieved after 6 weeks. The differential DR-FTIR spectra for 1, 3, and 6 weeks hydration of Belite/SP pastes are displayed in Fig. 4. It is not surprising to find here that upon addition of SP to the Belite paste, no visible amount of C-S-H has formed even after six weeks of hydration. This is partly due to the reduced amount of water included in the Belite/SP paste, but this negative result may also be taken to infer that the SP molecules coat the clinker particles, the surfaces of which become water repelling, and thus resistant towards clinker hydration.

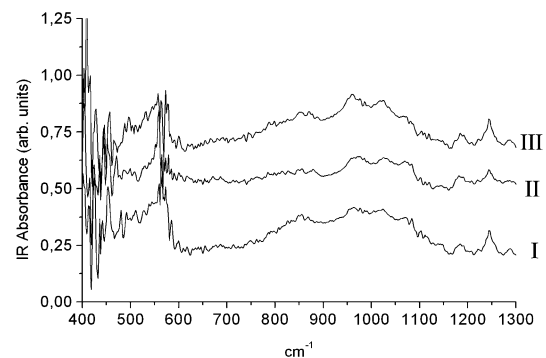


Fig. 4 DR-FTIR spectra of superplasticized Belite hydrated for 1 week (I), 3 weeks (II) and 6 weeks (III) after subtracting the spectrum of a 4 h hydrated superplasticized Belite sample

Initial hydration of Belite/SP/CNS

The accelerating effect on Belite hydration resulting from CNS addition was established in [Björnström and Panas, Submitted]. Whereas spectral saturation of a Belite paste was achieved after 6 weeks, the same result was obtained after some 24 h upon addition of 5% CNS. The ability of CNS to overcome the protective SP coating surrounding the Belite clinker particles can be appreciated in Fig. 5. While no product has started to form to any appreciable degree after 1 week, spectral saturation is arrived at after 3 weeks. Thus, while significantly slower than the Belite/CNS paste, adding 5% CNS to the Belite/SP paste is clearly seen to accelerate the initial hydration. The degree to which the Belite/SP/CNS paste is dormant during the first week of hydration may be better appreciated in Fig. 6, where the 4 h hydrated Belite/SP/CNS spectrum has been employed as reference. The absence of product signatures in the 1-week spectrum (VIII) comes out clearly. Equally well established is the fact that spectral saturation is achieved after 3 weeks of hydration. Thus, the rate of initial hydration of this paste is intermediate to the pure Belite and Belite/CNS pastes. Given a particular application, it is easy to foresee the potential here in the fine-tuning of this system for improved properties.

Modelling vibration spectra

We have chosen to associate the band which develops in the 800–1100 cm^{-1} region with the formation of calcium-silicate-hydrate. Still, it is obvious that the products formed during Alite and Belite hydration are not identical. In a previous work, we computed the vibrational spectrum of a subunit to the model C–

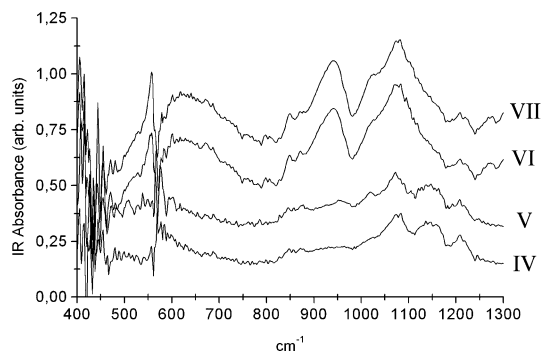


Fig. 5 DR-FTIR spectra of superplasticized Belite containing 5% CNS hydrated for 4 h (IV), 1 week (V), 3 weeks (VI) and 6 weeks (VII) after subtracting the spectrum of a 4 h hydrated superplasticized Belite sample

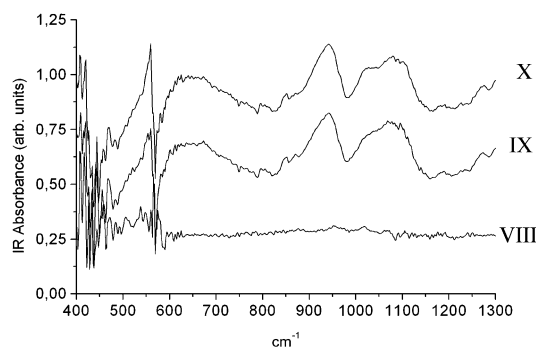
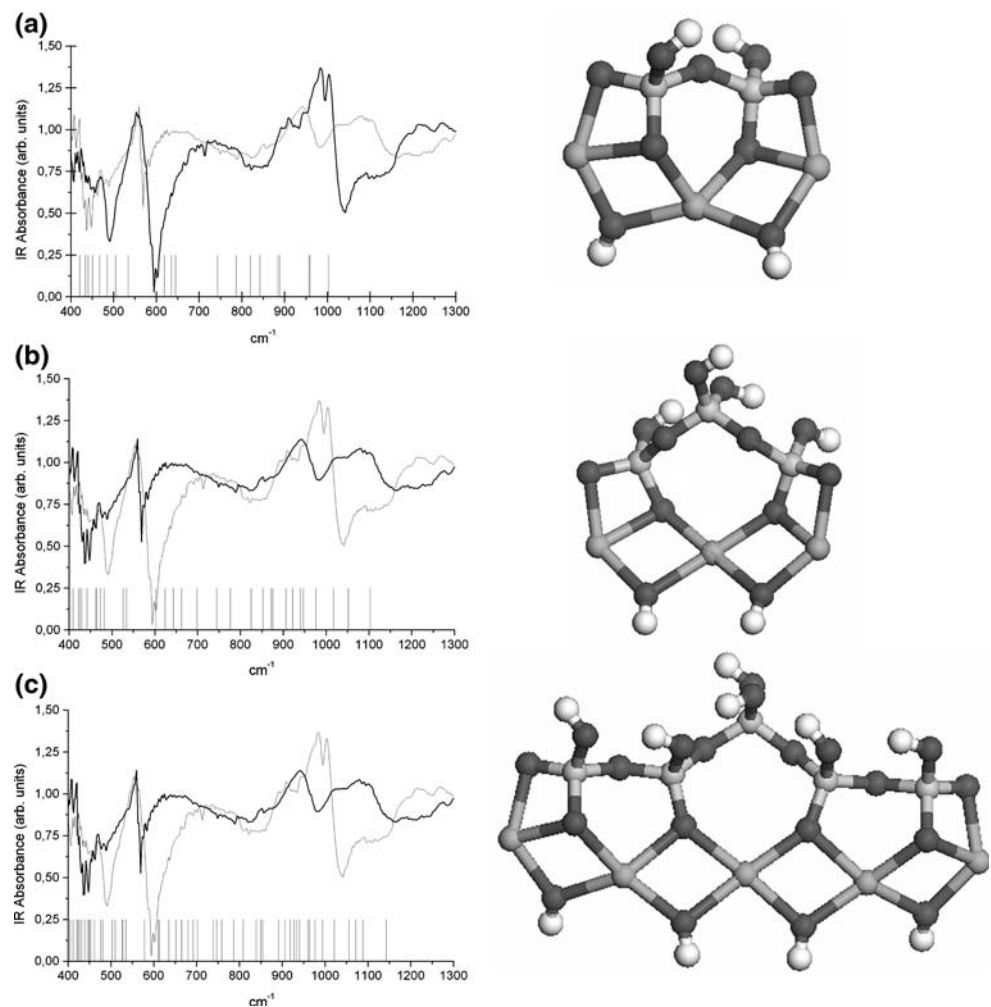


Fig. 6 DR-FTIR spectra of superplasticized Belite containing 5% CNS hydrated for 1 week (VIII), 3 weeks (IX), and 6 weeks (X) after subtracting the spectrum of a 4 h hydrated superplasticized Belite containing 5% CNS sample

S–H compound, Jennite, and it was indeed found to be consistent with the observed hydration product of Belite. It must be born in mind that the C–S–H is a composite material composed of $\text{Ca}(\text{OH})_2^{\text{poly}}$ and $\text{Ca}_x\text{Si}_y\text{O}_z$ subunits (cf. Richardson [12]) and that the stoichiometry of C–S–H is determined by the molar ratios of these constituents. Here, we test the hypothesis that the cause of the difference in the Alite and Belite C–S–H spectra is that short C–S–H clusters dominate the former and extended C–S–H clusters/polymers produce the latter. The series of ionic fragments $\text{H}_4\text{Ca}_3\text{Si}_2\text{O}_9$, $\text{H}_6\text{Ca}_3\text{Si}_3\text{O}_{12}$, and $\text{H}_{10}\text{Ca}_5\text{Si}_5\text{O}_{20}$ are displayed in Fig. 7, in conjunction with the spectra of the hydration products of Alite and Belite. It is observed that the larger oligomers display the highest frequencies, while down shifts are observed for the smaller fragments. While keeping the crudeness of the models in mind, it is indeed suggested that the rapid hydration of Alite results in an initial C–S–H product dominated by finite $\text{Ca}_x\text{Si}_y\text{O}_z$ fragments such as dimers. This is in contrast to Belite which would produce extended $\text{Ca}_x\text{Si}_y\text{O}_z$ polymers.

The morphological differences between C–S–H produced in Alite and Belite is consistent with the different strength development with time displayed by Alite and Belite based cements favouring the latter (cf. Popescu [13]). The reason for increased fragmentation of the C–S–H product in Alite as compared to Belite can be attributed to the difference in Ca/Si ratios, 3 and 2 for Alite and Belite respectively. Indeed, evidence for positive correlation between high Ca/Si ratio and short silicate chain lengths has been produced by means of NMR [14], which also tells that even after 26 years the chain lengths of C–S–H from C_3S is shorter than 5 [15].

Fig. 7 The computed spectra for clusters of increasing size are displayed together with the experimental Alite and Belite hydration product spectra. The bold experimental spectrum is suggested to display the better fit to the computed spectrum for each of the cases a–c



Concluding remarks

DR-FTIR spectroscopy was employed to monitor the product spectra during hydration of the clinker phases Alite and Belite. In both cases, retardation of the rate of hydration was observed upon addition of a polycarboxylate superplasticizer PC SP. Although the retardation effect of adding SP to cement is commonly seen (see e.g. ref. [1–5]), the representation of this effect by means of DR-FTIR is a main result of the present study.

(1) The rate of hydration of Alite in the absence of SP was monitored in [7], and it was actually too fast to allow for even a qualitative investigation. Here, addition of SP allowed the monitoring of reaction products over a 48 h time period. An initial transient product band was resolved for the first time, and seen to gradually transform into a final product band, interpreted to be composed of calcium-silicate-hydrate C–S–H. Upon addition

of colloidal nano-silica CNS to the Alite/water/SP system, the retardation effect was to some extent overcome. While all spectral features were found to be the same, their rate of inter-conversion was accelerated.

(2) Belite hydration was studied in [Björnström and Panas, Submitted], where it was found that product formation is initiated only after 2–3 weeks of hydration, and the DR-FTIR spectra saturate after about 6 weeks. Upon adding SP to the Belite/water paste, no signature of any hydration product formation was observed during the 6 weeks time period. Addition of 5% CNS to the Belite/water/SP system resulted in product formation after 2–3 weeks, with the same spectral characteristics as in the original Belite/water system. It becomes interesting to compare the rate of product formation in the Belite/water/SP/CNS system to that in the Belite/water/CNS, and Belite/water pastes. While spectral saturation is achieved after 3 weeks in the first, this is obtained

after 24 h in the second and after ~6 weeks in the Belite/water system.

- (3) Both the Alite and Belite product bands in the 800–1200 cm^{-1} region were suggested to originate from C–S–H formation. Differences in details of the product bands between the two clinker phases was associated with the formation of small C–S–H fragments in case of Alite, while extended C–S–H polymers were proposed to form upon Belite hydration. Quantum chemistry was employed here and in [Björnström and Panas, Submitted] to validate the consistency in this interpretation.

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