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# Insights into early hydration of Portland limestone cement from infrared spectroscopy and isothermal calorimetry

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ABSTRACT

Isothermal calorimetry and diffuse reflectance infrared DR–FTIR spectroscopy are combined to correlate evolutions of spectroscopic signatures with rates of chemical reactions as reflected in the rate of heat emitted during the first 38 h of cement hydration. Portland limestone cement mortar is employed and the analysis is repeated for two different mixing procedures. Intensive blender mixing with quartz sand is found to cause activation of the cement resulting in a faster hydration process. At early stages of hydration, two types of C–S–H are formed. The spectral intensity of the earlier C–S–H is found to saturate, while that of the later form continues to acquire intensity throughout the 38 h of the experiment. Evidences are presented which support the interpretation that the two forms differ mainly in morphology and water content. Simultaneously with the saturation of the early C–S–H, a transient species is observed with DR–FTIR. This species correlates with the observed thermogram fine-structure.

## 1. Introduction

The early stages of cement hydration are decisive for the ultimate performance of concrete. In general terms, early hydration essentially amounts to the conversions of clinker phases to various forms of calcium silicate hydrate, sulphates, and carbonates when adding water to cement. In order to understand how changes in mixing procedures or the addition of admixtures such as accelerators and super-plasticizers influences the long-term performance of cement based materials it is helpful to have simple and yet efficient time resolved methods for evaluating and for monitoring the various chemical processes taking place. The performance of DR–FTIR on the pure clinker phases [1,2], and in the study of very early stages of cement hydration [3,4] has been demonstrated previously. The objective of the present study is in part to demonstrate further the usefulness of DR–FTIR by addressing longer cement hydration times, and in part to demonstrate how complementary perspectives can be provided by combining infrared spectroscopy with isothermal calorimetry.

When Portland cement pastes are studied by isothermal calorimetry it is usually found that the thermograms consist of a very early peak, a dormant period, a second (main) peak (A in Fig. 1), and a small peak which usually appears after the maximum of the main peak (C in Fig. 1). The initial peak is the result of all processes taking place at the instance when the cement is mixed with water. The main peak is similar to the peak that one gets if one hydrates $C_3S$ (alite) – the main component of Portland cement – and it has therefore been attributed to the main reaction during hydration, i.e. the formation of C–S–H from $C_3S$ [5]. The origin of the subsequent peak has been attributed to the formation of ettringite from the aluminate phase [5,6].

Sulphate is added to all cements in the form of calcium sulphate. If sulphate is not added, the $C_3A$ and $C_4AF$ (aluminates) may quickly hydrate and cause flash set (loss of workability).

A Portland limestone cement containing about 15% limestone was employed in the present study. It has been shown previously that such cements have a different chemistry from ordinary Portland cements [8,9]. The addition of finely ground calcium carbonate – a fraction of which dissolves and takes part in the reactions – results in the formation of some monocarbonate instead of monosulphate, and influences the resulting AFm to AFt ratio [8].

Here diffuse reflectance infrared absorption spectroscopy is resorted to, in order to complement morphological studies based mainly on microscopy, and hydration rate studies based on isothermal calorimetry, with a cheap and easily available technique that is sensitive to changes in chemical bonding. Infrared absorption spectroscopy concerns wave length resolved photo-absorption, and it produces fingerprints of chemical bonding. Diffuse reflectance IR concerns multiple reflections of IR light prior to detection. Each reflection probes a certain area and a certain depth of a particle in a powder sample. If a sufficiently large amount of particles is considered, then the probability distribution of number of reflections, which a ray of light undergoes, is independent of the number of particles. In each reflection, the corresponding micro-particle is probed of the order of one wave lengths into its bulk. This corresponds to 10 μm for 1000 $cm^{-1}$ which is a typical wave number in the present study. Signatures of changes in composition of this scale, as

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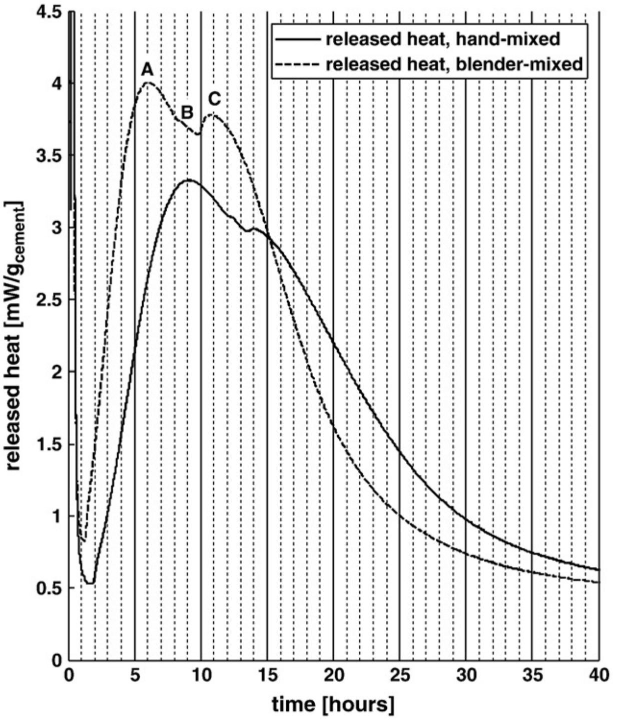

**Fig. 1.** Results from measurements with isothermal calorimetry on Portland limestone cement mortars made by hand mixing and mixed with a hand-blender.

reflected in changes in bonding due to hydration, are thus claimed to be accessed. Conversion of clinker materials into hydration products amounts to IR absorption intensity losses because of reactants' consumption as well as absorption intensity gains due to products' formation. In order to construct a differential spectrum, the raw spectrum taken at a reference time is subtracted from the raw spectrum acquired at a later time. The reason for why this procedure works is because the dielectric function, which describes how a sample is polarized by incoming light, is slowly varying with wave number. Small changes in the mounting of the powdered sample do not have significant impact on this function, while changes in amount of powdered sample cause constant parallel shifts in the dielectric function. This is in contrast to the vibrational excitations, specifically addressed in the present study, which are local objects and negligibly affected by either of the two mentioned parameters. This overall understanding was validated in [3] where the DR–FTIR absorption spectra of equivalently produced mortars from different batches, which were allowed to cure from the same time, were subtracted and demonstrated to produce an almost flat and structure-less differential spectrum. The potential usefulness of this approach was demonstrated in [1,4]. The generality of differential DR–FTIR spectroscopy can be appreciated by considering the sulphition and sulphation studies on calcareous stone [10].

The main objective of the present study is the identification of spectral signatures of each of the peaks seen in the calorimetric results by means of DR–FTIR. This is done by correlating the time evolutions of absorption bands to what is observed by means of isothermal calorimetry. It is proposed that by this we are able to distinguish whether the two-peak signatures in the calorimetric measurements reflect two unrelated chemical processes or two consecutive processes for the same overall reaction.

## 2. Method

A calorimetric instrument was specially designed for this study. It contained two isothermal heat-conduction calorimeters for 20 mL vials of a similar type as described in Wadsö (2005) [11] and Lamprecht et al. (2009) [12]. The calorimeters were placed in a thermostat whose temperature was controlled by a thermoelectric air–air heater/cooler (AA-100-24-22, SuperCool AB, Göteborg, Sweden). The thermostat was arranged so that several more samples in 20 mL ampoules could be placed in the thermostat, and removed without opening the thermostat.

Mortars were made from 300 g Portland limestone cement (CEM II/A-LL 42.5, "Byggcement Skövde", Cementa AB, Sweden), mixed with 240 g fine quartz sand. A particularly fine sand was chosen because then the sand particles don't have to be crushed when grinding the samples for DR–FTIR measurements. Then 150 g of deionized water was added (w/c = 0,5). The mortar was mixed for one minute by hand in a small beaker. Several samples (5–10 g) were then taken out and placed in 20 mL plastic vials. The rest of the mortar was then mixed for 5 min with a hand-blender. To keep the temperature constant at around 20 °C the beaker was dipped in an ice-bath when needed. After mixing several samples were again taken and placed in plastic vials.

One vial from each mixing procedure was placed in the calorimeter and the remaining vials were placed in the calorimeter thermostat to ensure that they were exposed to the same conditions as the samples that were measured on in the calorimeters. Samples were taken at different hydration times, i.e. after 15 min of hydration, then every 2 h up to 22 h and at 27, 31 and 38 h. Only a selection of spectra, representative of the hydration process is presented in the paper. One sample from each mixing procedure was taken out of the compartment and the hydration was stopped by immersion of the samples in liquid nitrogen. The samples were then freeze-dried over-night. The next day the samples were ground and measurements with DR–FTIR were performed. The spectrometer used was a Nicolet Magna-IR 560 with an insert cell for diffuse reflectance spectroscopy. The measurement range lies between 400 and 4000 $cm^{-1}$.

Reported differential spectra, defined relative to a reference spectrum acquired at a given time, are employed in order to emphasize any chemical changes due to further hydration. Thus, products formed after the reference time come out as positive peaks and consumed reactants appear as dips in the resulting spectra.

## 3. Results

### 3.1. Calorimetry

The calorimetric measurements are shown in Fig. 1. Similar overall signatures are observed for the hand-mixed and blender-mixed samples, though the process is significantly accelerated in case of the latter. This is seen in the narrowing of peaks in conjunction with increased heights for the blender-mixed samples, even if the total amounts of heat given off during the first 40 h are similar, as seen in Fig. 2. Interestingly, besides the dominating two-peak characteristics, an intermediate shoulder is observed in both types of samples. Thus, the calorimetry results show three maxima at 9, 12, and 14 h of hydration (hand-mixed) and at 6, 9 and 11 h of hydration (blender-mixed), respectively. In what follows, these are named A, B and C, respectively.

### 3.2. Diffuse reflectance infrared spectroscopy

The three chemical processes observed by the calorimetric measurements, were analyzed by DR–FTIR on the cement samples that were removed at different times from the calorimetric thermostat. The time evolution of spectral intensities for the hand-mixed samples can be seen in Fig. 3, using the spectrum corresponding to 2 h of hydration as reference. 2 h of hydration was chosen as it lies in the dormant period where little chemical changes occur. Clearly, there are four major contributions to the spectra, i.e. at 1000 $cm^{-1}$ (*i*), at 1300 $cm^{-1}$ (*ii*), at 1650 $cm^{-1}$ (*iii*) and at ~3000–3500 $cm^{-1}$ (*iv*).

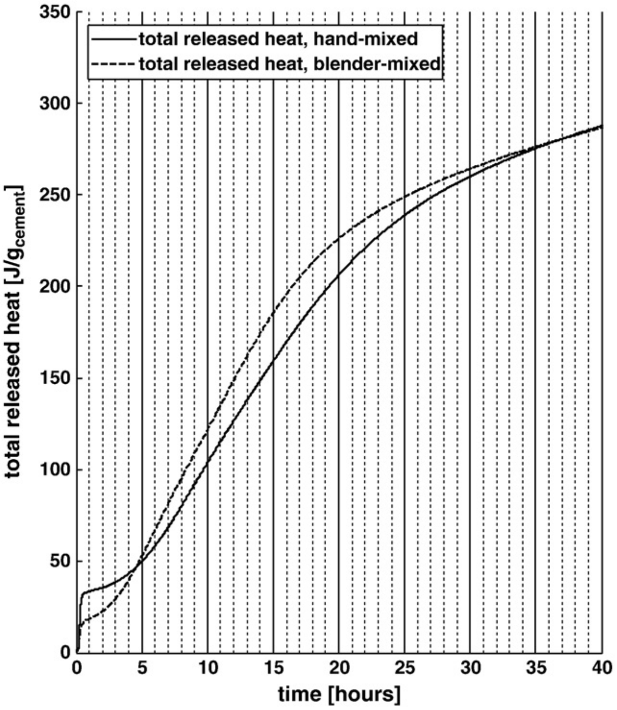

**Fig. 2.** Integration of the curves given in Fig. 1, displaying the total heat given off by each sample at hydration times up to 40 h.

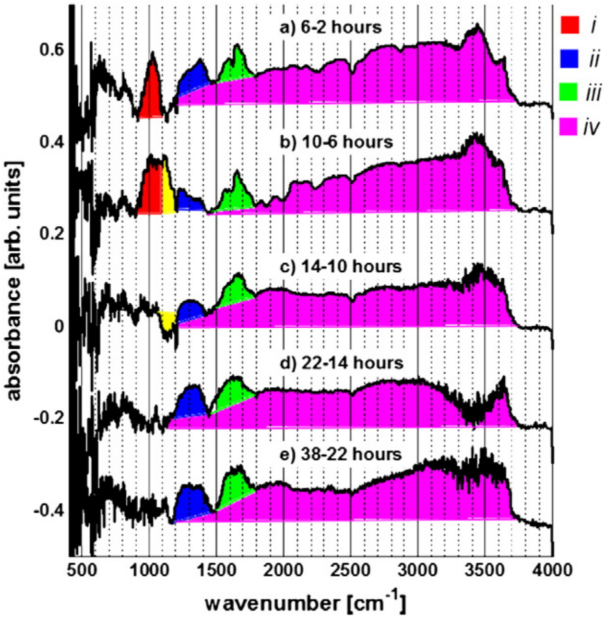

**Fig. 4.** The incremental, time resolved formations of hydration products in the hand-mixed mortar samples are reported, as seen by means of DR–FTIR difference spectra. Changes in products formed at different stages of hydration emerge by taking consecutive difference spectra. The spectra are deliberately offset to improve readability. The colours are only a guide for the eye. The signature of the transient compound is marked with yellow.

Moreover, it appears that the species *i* saturates in the vicinity of the maximum of the first calorimetric peak, while species *ii*–*iv* continue to grow during the full 38 h of the experiment. To see the spectral signatures developed during different stages of hydration, the spectrum taken at the beginning of the period can be subtracted from the spectrum at the end of the period. Thus only the changes taken place during the period will be seen. Separation of different processes during cement hydration is made possible by investigating changes in the spectra during a pre-selected time interval. This is done for the hand-mixed sample in Fig. 4 and the blender-mixed sample in Fig. 5. Band *i* increases in intensity only in the 2–10 h time interval

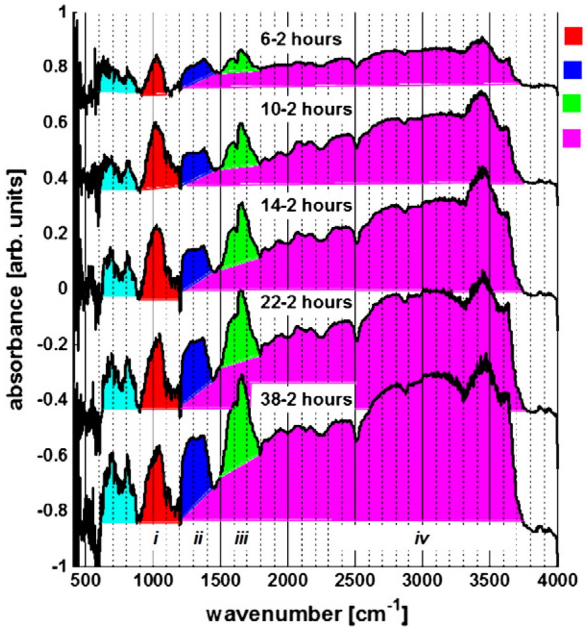

**Fig. 3.** DR–FTIR difference spectra for the hand-mixed mortar are displayed. These are obtained by subtracting, from the spectrum acquired after each time of hydration, the reference spectrum acquired at 2 h. The spectra are deliberately offset to improve readability. The colours are only a guide for the eye.

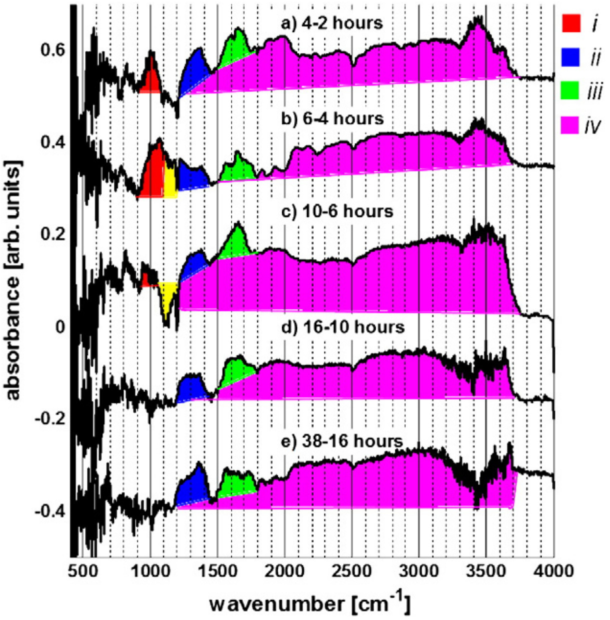

**Fig. 5.** The incremental, time resolved formations of hydration products in the blender-mixed mortar samples are reported, as seen by means of DR–FTIR difference spectra. Changes in products formed at different stages of hydration emerge by taking consecutive difference spectra. The spectra are deliberately offset to improve readability. The colours are only a guide for the eye. The signature of the transient compound is marked with yellow.

for the hand-mixed sample, while for the blender-mixed sample this time interval is reduced to 2–8 h. Band *ii*, *iii* and *iv* grow continuously during the whole hydration process. In additional there is a band at 1100–1200 $cm^{-1}$ which gains intensity over the 6–10 h time interval for the hand-mixed sample. For the blender-mixed sample this signature is found at the 4–8 h interval. This absorption appears as a broadening of band *i* in spectra 4b and 5b. In spectra 4c and 5c a dip in this region is seen instead, indicating that whatever was formed in the preceding time interval has disappeared during this time interval.

## 4. Interpretation of results

Bands *iii* and *iv* at 1650 $cm^{-1}$ and at ~3000–3500 $cm^{-1}$ are associated with incorporation of water in the matrix, i.e. from H–O–H bend and HO–H stretch vibrations, respectively [13–15]. The band *i*, at 900–1100 $cm^{-1}$, was previously described in Portland limestone cement [4], and said to correspond to Si–O asymmetric stretch in an early form of C–S–H [14,16–18]. This conclusion finds further support in the correlation of this band with the growth of two bands slightly below 700 $cm^{-1}$ and slightly above 800 $cm^{-1}$ (Fig. 6). These bands are also found in C–S–H, and are said to correspond to the Si–O–Si bending and Si–O symmetric stretch modes, respectively [16–18]. While these and the bands at 900–1100 $cm^{-1}$bands cease to grow after some 10 h, the continuously growing band *ii* at 1200–1400 $cm^{-1}$ becomes the increasingly more dominant one during the later stages of the 38 h hydration measurements (Fig. 3). It is possible to isolate the spectral signatures of this band by producing the difference between the spectra at 38 h and 14 h (38 h and 10 h in case of the blender-mixed sample). It is gratifying to note how the growing C–S–H bands are complemented by the continuous dissolution of alite as observed in absorbance losses at ~600 $cm^{-1}$ (see Fig. 3 again).

The DR–FTIR signature of the intermediate shoulder, observed for both hand and blender-mixed mortars (B in Fig. 1) is correlated with a broadening of band *ii* in spectra of Figs. 4b and 5b. Interestingly, if this spectral feature is taken to signify formation of a new hydration product, a dip in the same spectral region is observed in the following hours (Figs. 4c and 5c) as would it reflect the dissolution of the very same hydration product. The appearance and disappearance of the band in the 1100–1200 $cm^{-1}$ region suggest that it was due to sulphates [19]. In particular, the signature does not contain any peaks unique to crystalline compounds and is therefore taken to reflect a transient of amorphous nature.

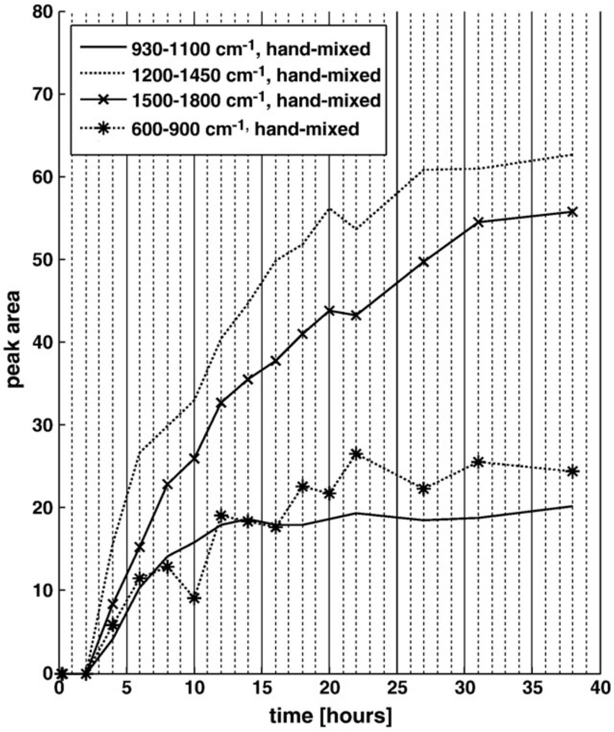

**Fig. 6.** Integration of selected bands in the DR–FTIR spectra of the hand-mixed mortar with 2 h as reference (some of these spectra are displayed in Fig. 1).

## 5. Discussion

Throughout the present study, comparisons are made between calorimetric thermograms and DR–FTIR. Consistencies in timings of the different techniques with regard to appearances and disappearances of characteristic features are reported. In order to test for accidental agreements, the analyses were repeated for two different mortar mixing procedures. Thus, intensive mixing results in significantly faster hydration. Two possible causes for this are the breaking of cement particle aggregates [20] and the erosion of early formed compounds on the surfaces of the as received cement grains. The effect of intensive mixing is significantly more pronounced when sand is added [21] as was done in the present study. The sand is understood to work as a blasting aid, increasing the erosion of clinker surfaces. The sand also collides with agglomerates and increases the desagglomeration. The resulting clinker particles obtained by the intense mixing are found to dissolve faster and arrive earlier to each stage in the hydration process. This is consistent with the fact that upon integrating the calorimetric curves, it is found that the heats produced (up to 38 h) are similar for the two preparation techniques, indicating that the same amount of clinker is dissolved, but at different rates. The erosion of surfaces increases dissolution of clinker in the mortar and thus shortens the induction period. The increased surface obtained by desagglomeration allows the hydration products to be more widely distributed, resulting in thinner shells around the clinker particles and thus less transport resistance for the same amount of products, increasing hydration rate at later stages.

Taylor [22] discusses several different forms of C–S–H being formed during the hydration of $C_3S$. The C–S–H formed early requires much space as it is characterized by fibrous outgrows from the cement grain. It is termed “C–S–H type I”. Subsequently, one or several denser forms of C–S–H termed “C–S–H type II–IV” are formed. Observation of “C–S–H type I” by means of DR–FTIR was made in [4] employing SEM as complementary technique. It was associated with a DR–FTIR absorption band at 1000 $cm^{-1}$. This band is clearly seen in the present study as well (c.f. Fig. 3). Thus, a build-up of IR bands corresponding to silica oligomers at ~1000 $cm^{-1}$ in conjunction with accumulation of water is observed. Interestingly, the growth of the band at ~1000 $cm^{-1}$ as well as its saturation is correlated with the time evolutions of the first peaks in the thermograms of both hand-mixed and blender-mixed mortars. These correlations in times can be taken to support any hypothesis which has “C–S–H type I” as major product during the early hydration stage.

After the maxima of the main heat evolution peak (A) formation of “C–S–H type I” comes to a halt. This is seen in the difference spectra acquired beyond the maximum of the main heat evolution peak. These spectra display minor changes in absorption intensities in the silica associated region of early C–S–H (~1000 $cm^{-1}$) (Figs. 4 and 5). Simultaneously with the appearance of C–S–H type *i* in the DR–FTIR spectra, a novel second band is seen to develop at 1200–1350 $cm^{-1}$. This species is consistent with the observations of Taylor regarding the formation of a more compact C–S–H product i.e. “C–S–H type II” (*vide supra*). Hence, while the formation of “C–S–H type I” comes to a halt or reaches steady-state conditions, the compact form of C–S–H continues to form throughout the whole experiment.

In the thermogram, in the vicinity of peak A, a new species starts to form as signified by a band at ~1100–1200 $cm^{-1}$ (see spectra in

Figs. 4b and 5b). However, at a later time this absorption band vanishes. Given that sulphates absorb in the region between 1100 and 1200 $cm^{-1}$ [19,23,24], this could possibly be a sulphate based species, although a silicate based species cannot definitely be ruled out. The possible origins of these transient bands, are discussed in some detail in [25]. Here, it is emphasized that while said assignments are somewhat ambiguous, the same appearance and disappearance of these bands are observed both for the hand-mixed and blender-mixed mortars. Were this to signify transient sulphate conversion, it would be in line with the general understanding of the role of gypsum as additive in cement. Thus, it has been frequently proposed that the shoulder on the main peak in the thermogram (peak C) is caused by dissolution of aluminate phases e.g. C3A, which become reactive at this stage due to reduction in sulphate concentration in the pore solution [7]. It is implied that suppression of sulphate concentration, the presence of which in the first place was to block aluminate dissolution, allows for C3A dissolution and subsequent formation of ettringite. The fact that addition of sulphate controls the rate of aluminate hydration, is central to the interpretation of the shifts in position and magnitude of peak C as function of the amount of sulphate added [26].

In order to learn which spectral signatures are correlated in time, the DR–FTIR absorption peaks were integrated, see Fig. 6, omitting the O–H stretch and transient bands at 3000–3500, and 1100–1200 $cm^{-1}$, respectively. Here, an additional domain in the DR–FTIR spectrum at 600–900 $cm^{-1}$ is included in the analysis, besides those at 1000, 1100–1200, 1200–1350, 1600–1800, and 3000–3500 $cm^{-1}$. Interestingly, the spectral features at 600–900 and at 1000 $cm^{-1}$ are strongly correlated in time which suggest these to refer to the same chemical compound, while the 1200–1350, and 1600–1800 $cm^{-1}$ bands appear to display signatures of a second compound. We propose that the pair of bands at 600–900 and 1000 $cm^{-1}$ reflects common signatures of C–S–H types I and II. By combining the DR–FTIR results with the micrographs of Scrivener [27] acquired after comparable times of hydration, it is concluded that the morphological changes which dominate at hydration times greater than 12 h do not affect these two bands. Rather, the morphologically different hydration products differ in the amount of water they incorporate. This conclusion is based on the integrated absorption bands at 1200–1350, and at 1600–1800 $cm^{-1}$, of which the latter is known to be associated with H–O–H bending vibration mode, and the former parallels the latter in quite some detail.

It is tempting to formulate a possible overall understanding and possible consequences of the observations. Apparently, rapid early formation of “C–S–H type I” becomes water transport limited due to the formation of a C–S–H scale. C–S–H type I is continuously converted into C–S–H type II. Strain in the C–S–H type II scale increases with increasing density to the point when cracks appear, which allow re-entry into the original non-transport limited hydration process. This transition is reflected in a transient feature at ~10–14 h observed by DR–FTIR as well as in the thermograms where a small depression in heat release is followed by a sudden increase. Based on the DR–FTIR, C–S–H type I is formed rapidly while being continuously transformed into C–S–H type II at a slow but constant pace during the full time span of the experiments.

## 6. Conclusions

Isothermal calorimetry and DR–FTIR have been employed to monitor early hydration of a Portland limestone cement mortar. It was demonstrated that the combination of these techniques complemented with electron microscopy [4,26] gives complementary information and insights into the early hydration process. Calorimetry is a straightforward method to obtain information about *when* something is happening. DR–FTIR can then be employed to get insight as to *what* chemical processes are involved. Electron microscopy gives information regarding changes in morphology.

DR–FTIR signatures of two forms of C–S–H were reported, characteristic of “C–S–H I” and “C–S–H II”. The former is formed predominantly at early stages and is found to transform into the latter during the first 38 h of hydration. This transformation is mainly morphological in nature. It is characterized by the change of the water content of the C–S–H. The saturation time of characteristic silica bands at 600–900 and 930–1100 $cm^{-1}$ correlates with the appearance of a transient species. Appearance and disappearance of this transient species are observed by means of DR–FTIR, and are correlated with a fine-structure in the thermogram. This scenario is observed both for a hand-mixed mortar and a blender-mixed mortar, although at different times. This is because the intense mixing of the blender accelerates hydration.

In summary, a practical way to employ DR–FTIR has been demonstrated, and shown to provide complementary information to well accepted techniques in the study of cement hydration.

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