



## Early hydration and setting of Portland cement monitored by IR, SEM and Vicat techniques

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### ABSTRACT

Diffuse Reflectance Infrared DR-FTIR spectroscopy is employed to monitor chemical transformations in pastes of Portland limestone cement. To obtain a sufficient time resolution a freeze-dry procedure is used to instantaneously ceasing the hydration process. Rapid re-crystallization of sulphates is observed during the first 15 s, and appears to be complete after ~30 min. After ~60 min, spectroscopic signatures of polymerizing silica start to emerge. A hump at 970–1100  $\text{cm}^{-1}$  in conjunction with increasing intensity in the water bending mode region at 1500–1700  $\text{cm}^{-1}$  is indicative of the formation of Calcium Silicate Hydrate, C-S-H. Simultaneously with the development of the C-S-H signatures, a dip feature develops at 800–970  $\text{cm}^{-1}$ , reflecting the dissolution of Alite,  $\text{C}_3\text{S}$ . Setting times, 180 (initial) and 240 (final) minutes, are determined by the Vicat technique. Combining DR-FTIR, SEM and Vicat measurements it is concluded that the setting is caused by inter-particle coalescence of C-S-H.

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### 1. Introduction

Today, Portland cement is a widely used binder in concrete construction.  $\text{C}_3\text{S}$  (alite) and  $\text{C}_2\text{S}$  (belite) is essential to the build-up of strength in Portland cement. These two calcium-silicate phases are formed above 800 °C, where  $\text{C}_3\text{S}$  is preferentially formed upon elevating the temperature and increasing amount of added burned lime, CaO.  $\text{C}_3\text{S}$  is responsible for short term strength development (days to months) while  $\text{C}_2\text{S}$  displays the better long term strength development performances (~years). The quest for increasingly shorter setting time and early strength has seen the  $\text{C}_3\text{S}/\text{C}_2\text{S}$  ratio increase in commercial Portland cement. In recent years, the increased attention on environmental aspects of material conversion has influenced research towards possible modifications of Portland cement to better meet the increasing demands for sustainability in the construction sector. This is done by using additives and changing the composition of the cement. Many different experimental techniques have been employed to investigate the effects on material conversion as Portland cement is dissolved and transformed into calcium-silicate-hydrate, C-S-H. For determination of setting times, Vicat measurements are often employed. At later stages in the hydration process, an ultrasonic cement analyser may be used to determine changes in the elastic modulus of the mortar [1,2]. Calorimetry is employed to monitor the heat released upon hydration [3–7], whereas X-ray diffraction [8–13], nuclear magnetic resonance [14–16] and Fourier transform infrared spectroscopy, FTIR, are used to

obtain chemical information. Morphological information may be obtained by means of scanning electron microscopy and transmission electron microscopy [11,12,15,17].

Spectroscopic methods are commonly used to study the chemistry of cement hydration. In the present work the hydration of Portland cement has been monitored mainly by means of infrared spectroscopy. In infrared spectroscopy one utilizes that molecules or groups of atoms on large molecules absorbs different wavelengths of infrared light depending on which atoms that constitute the molecule or group, its geometry and its immediate surroundings. It can therefore be used to study both crystalline and amorphous samples. The sample is irradiated with infrared light with a span of different wavelengths. The sample will absorb some of the light at wavelengths that are characteristic to its chemical composition. To see at which wavelengths the sample has absorbed light the intensity at each wavelength is measured with and without sample. IR radiation only penetrates about 1 wavelength into the sample (~10  $\mu\text{m}$  for 1000  $\text{cm}^{-1}$ ), making it ideal in the study of surface processes.

In previous studies where FTIR was used to study the hydration of cement and its components, the sample was prepared by mixing the cement with KBr and pressing the mixture into pellets [18–21]. The usefulness of Diffuse Reflectance Fourier Transform Infrared Spectroscopy, DR-FTIR, as a tool for studying the hydration of cement has also been demonstrated in previous work [22,23]. A comparison between DR-FTIR and the KBr pellet technique has been done by Delgado et al. [24], who showed that the methods produce similar spectra. The advantage of the KBr technique is that it provides better defined bands than DR-FTIR, but the sample preparation is more labour intensive. The results of the present study suggest that the DR-FTIR technique employed is indeed

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preferred in that external physico-chemical interference is minimized, i.e. the hydration products are studied in the proper cement matrix with a minimum of sample tampering, and avoiding contact with foreign chemicals. Differential IR light absorption of samples which have been allowed to hydrate for different times is reported here.

Water displays strong absorption in the mid-IR range, which makes it virtually impossible to perform *in situ* studies of cement hydration. A second drawback of *in situ* DR-FTIR for the study of cement hydration is that the surface of the cement paste, while hydrating, may become too flat for the diffuse reflectance technique to be efficiently used. These considerations validate selection of an *ex situ* DR-FTIR approach.

To study very early hydration using an *ex situ* technique, it is imperative that the hydration is stopped instantaneously at a predetermined time. To satisfy this requirement, a freeze-dry technique is adopted in this research. The freezing of the sample with liquid nitrogen ensures that all chemical processes are very much retarded, while the subsequent water evaporation step at low temperature minimizes any thermally induced chemical transformations other than water removal while drying. Indeed, earlier microscopy work [25–27] has shown that freezing is a relatively mild method to stop hydration. The drying will of course affect the structures of some phases. Bound water, like in ettringite, could be partially removed, and morphological properties may change upon removal of water.

The purpose of the present study is to demonstrate the efficiency of the freeze-dry procedure in conjunction with DR-FTIR spectroscopy for studying the complex hydration chemistry of Portland cement. An attempt to correlate relevant spectroscopic signatures to the development of strength in the system is also made. Strength development is monitored here by means of Vicat measurements.

## 2. Experimental

The Portland cement used was a Portland limestone cement, “byggcement Std PK Skövde CEM II/A-LL 42,5 R”, from Cementa AB. An automatic/manual mortar mixer 39-0031 from ELE International was used. The cement was mixed with distilled deionized water that was poured into the mixing bowl before adding the cement. The ratio of water to as received dry cement was 0.4 by weight in both DR-FTIR and Vicat measurements. The cement was carefully added and the paste was mixed at 140 rpm on the mixing blade and 62 rpm on the mixing head. The hydration time was measured from the instant when the cement was added to the water.

### 2.1. DR-FTIR

The spectrometer used was a Nicolet Magna-IR 560 with an insert cell for diffuse reflectance spectroscopy. The measurement range lies

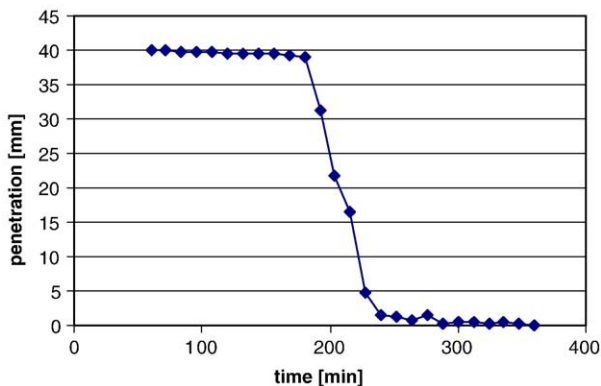


Fig. 1. Vicat measurement showing the depth of penetration of the Vicat needle into the cement as function of time. The height of the mould was 40 mm.

Table 1

Possible assignment to some of the peaks observed in Figs. 2–5.

Wave number [cm <sup>-1</sup> ]	Possible assignment	Reference
656–658	$\nu_4$ of SiO <sub>4</sub>	[21,40]
714	$\nu_4$ of CO <sub>3</sub>	[22,32,35,37]
847–848	Al–O, Al–OH	[21,35]
877–878	$\nu_2$ of CO <sub>3</sub>	[21,22,35,37]
1011–1080	Polymerized silica	[19]
~1100–1200	$\nu_3$ of SO <sub>4</sub>	[19,22,31,32]
1200–1202	Syngenite, thenardite	[32–34]
1400–1500	CO <sub>3</sub>	[19,21,22,35,37]
1620–1624	$\nu_2$ of water in sulphates	[22,31,33]
1640–1650	$\nu_2$ H <sub>2</sub> O	[21,35,36]
1682–1684	$\nu_2$ of water in sulphates	[22,31,33]
1795–1796	CaCO <sub>3</sub>	Own measurement, [22]
2513–2514	CaCO <sub>3</sub>	Own measurement, [22]
2875–2879	CaCO <sub>3</sub>	Own measurement, [22]
2983–2984	CaCO <sub>3</sub>	Own measurement, [22]
3319–3327	Syngenite, thenardite	[32–34]
3398–3408	$\nu_3$ of H <sub>2</sub> O, capillary water	[36]
3457	$\nu_1 + \nu_3$ of H <sub>2</sub> O	[21,36]
3554	$\nu_3$ of H <sub>2</sub> O in gypsum	[22,31]
3611	Bassanite	[22]
3641–3644	Ca(OH) <sub>2</sub>	Own measurement, [20,23,24,37]

between 400 and 4000 cm<sup>-1</sup>. The diffuse reflectance technique is utilized, in which the incident beam is allowed to be reflected off the ground sample towards an overhead mirror upon which the diffusely scattered rays are collected and measured in the detector. A more detailed description is given by Fuller and Griffiths [28]. The sample is scanned 64 times with a resolution of 2.0 cm<sup>-1</sup> and the presented data is an average value. Each sample was prepared and analyzed 3 times and the final spectrum was an average of these 3 measurements to minimize differences due to sample preparation.

The batch size was 200 g of as received dry cement. As the cement hydration was studied from 15 s the cement paste was only mixed for 15 s. However, the chemical development of the cement paste was found to be insensitive of mixing time as long as the cement was completely wetted [29]. Samples were prepared in plastic dishes of 35 mm in diameter. The thickness of the paste in the dishes was ~2–3 mm. Lids were placed over the dishes while they hydrated to prevent water from evaporating. The samples were hydrated between 15 s and 360 min in normal laboratory environment, then frozen by immersion in liquid nitrogen and subsequently placed in the freeze drier overnight. Measurements were made the following day. Before measurement the sample was ground and placed in the sample holder of the DR-FTIR spectrometer. To obtain good reproducibility, great care was taken when grinding the samples and placing them in the sample cup to make the samples as similar as possible.

### 2.2. Vicat

The batch size was 300 g of as received dry cement and the cement paste was mixed for 2\*90 s with a stop in between for 15 s to scrape the paste from the inside walls. The Vicat apparatus used was a Vicatronic automatic recording apparatus E040 and measurements were performed in a 40 mm mould with a calibrated weight of 300 g and a cylindrical needle with flat tip area of 1 mm<sup>2</sup>.

### 2.3. Scanning electron microscopy

The microscope used was a FEI Quanta 200 FEG ESEM operated in secondary electron detection mode with high-vacuum and an acceleration voltage of 2 kV. Some of the freeze-dried samples were pulverized. Since the freeze-dried samples were barely holding together this was easily done with a metal spoon. Some of the powder was placed on carbon tape attached to the sample holder.

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