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In-situ monitoring of early hydration of clinker and Portland cement with optical fiber excitation Raman spectroscopy

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Abstract

This paper explores the potential of using optical fiber Raman spectroscopy for continuously monitoring the early hydration of cement thanks to its superb capacities for characterizing wet samples and poorly-structured calcium-silicate-hydrate (C-S-H) as well as its excellent remote sensing competence. A bespoke optical fiber excitation Raman spectrometer with a 632.8nm laser wavelength under an "optical fiber excitation + spectrometer objective collection" configuration was established and applied. The ongoing hydration of a clinker and a Portland cement (PC) was then monitored during their first 8 hours of hydration. The main hydration products, in particular, C-S-H and ettringite & monosulfate (AFt & AFm), have been successfully identified and continuously monitored *in situ*. The findings from the optical fiber Raman were well supported by bench-mounted Raman, X-ray Diffraction (XRD) and Isothermal Conduction Calorimetry (ICC) tests. The results presented in this paper show a great potential of optical fiber Raman spectroscopy for future civil engineering applications.

Keywords: Bench-mounted Raman spectroscopy; Cement; Clinker; Hydration; Optical fiber excitation Raman spectroscopy

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1. INTRODUCTION

Cement hydration is a rather complex process (the notations used henceforth are C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, Š=SO_3, H=H_2O), which involves a series of chemical reactions between the various anhydrous minerals (i.e. C_3S, β-C_2S, C_3A & C_4AF) and water in the presence of gypsum to yield hydration products, which, in turn, is associated with the physical-mechanical changes of cement matrix over time. Briefly, two significant series of reactions occur during the hydration of cement. One is the reactions between C_3S (Alite) or β-C_2S (Belite) and water to yield calcium silicate hydrate [$CaO_x.SiO_2.H_2O_y$, C-S-H], i.e. C-S-H gel, and calcium hydroxide [$Ca(OH)_2$, CH] [1-3]. The other reaction involves C_3A or C_4AF which reacts first with calcium sulfate and water to yield calcium aluminate trisulfate hydrate (ettringite, AFt) with a typical formula of $C_6A\check{S}_3H_{32}$ or $C_6(A,F)\check{S}_3H_{32}$, and it then reacts with the residual C_3A after full-consumption of calcium sulfate to yield monosulfate hydrate (AFm, $C_4A\check{S}H_{12}$ or $C_4(A,F)\check{S}H_{12}$) [1-3]. Accordingly, the hydration of Portland cement (PC), based on its heat evolution, is empirically treated as four stages, i.e. pre-induction period (first few minutes), induction period (first few hours), acceleration period (3-12 hours) and post-acceleration period (after 12 hours) [1-3]. However, although the different stages associated with the hydration have been well established, the mechanisms and kinetics of the hydration is still under debate, in particularly the onset and termination of the induction and acceleration period during early hydration. Due to the importance of hydration reaction to the properties of concrete, extensive research has been undertaken worldwide in the past to investigate the nature of the hydration reaction. Characterization techniques such as X-ray Diffraction (XRD)、Isothermal Conduction Calorimetry (ICC)、Thermogravemitry (TG) and Scanning Electron Microscope (SEM) have therefore been widely employed for this purpose [4-8]. Whilst some useful information can be obtained, each of these techniques suffers from some limitations. For example, while XRD can be used to characterize various crystalline phases in both anhydrous and hydrated substances, such as C_3S, C_2S, CH and AFt, its capacity in characterizing C-S-H gel is very much limited. ICC, on the other hand, can provide certain information about the hydration process by illustrating the on-going heat generation, but has limited use in identifying the chemical reactions as well as the contributions from each mineral during the hydration process.

Compared to the aforementioned techniques, the solid-state Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) is a powerful tool capable of characterizing a variety of analytes regardless of their states (well-crystalline, poorly ordered or amorphous phases), allowing probing the local atomic-level compositions, structures and site connectivities of different species [9]. This technique, particularly the ^{29}Si MAS NMR, is widely used in cement and concrete area to investigate different silicate environments in the C-S-H hydrates, providing useful information to elucidate the molecular structures and lengths of silicate chains in the C-S-H [9-11]. Furthermore, as a well-established technique, the quantifying protocol of MAS NMR has also been widely employed by using an internal reference and considering the integrated intensities of the spectra calibrated with respect to the reference [10]. Nonetheless, the sample preparation of NMR is too complicated for the practical applications. Additionally, the spatial resolution of the commonly available instrument is only at micron-level which is also insufficient for some practical applications. On the other hand, due to the low sensitivity and low concentration of the most important spin nuclei in the real cementitious materials, the quality of signal is an issue and, therefore, a long instrument data collection time is normally required to obtain reasonable signal quality [10, 12], which is again not ideal for certain applications. Additionally, the large centrifugal forces of MAS NMR could lead to a heterogeneous distribution of water and solids in the rotor and consequently concerns could be raised when NMR is used to study the cement hydration [12]. To achieve a better understanding on the hydration reaction, researchers have been exploring techniques that are more sophisticated, easy for sample preparation and also be possible for future real engineering applications.

Raman spectroscopy, since 1970's, is increasingly applied in cement and concrete research [13-16]. Particularly, its applications in identifying the anhydrous cement/clinker minerals (C_3S, β–C_2S, C_3A and C_4AF) as well as their hydration phases (CH, C-S-H, AFt and AFm), have attracted considerable attentions [17-23]. Moreover, its superb capacity in recognizing both poorly-crystallized phases, such as C-S-H gel, as well as crystalline phases, such as AFt, makes it a much-desired technique for investigating hydration process. However, previous Raman studies were mostly undertaken to characterize the hydrated samples after the hydration being stopped using solvent or freeze drying methods. Compared to other techniques used for characterizing cement hydration, even though the Raman spectroscopy is a surface sensitive technique, in particular useful for characterizing just a few microns in depth [24, 25], it also has some additional advantages, including no special sample preparation requirements, as well as its superior capability in analyzing liquid/wet samples [26, 27]. Most importantly, compared to MAS NMR, Raman spectroscopy is more suitable for analyzing wet samples *in situ* without causing any interference to the status of the sample. This feature of Raman spectroscopy is an obvious advantage over MAS NMR, in particular for studying the hydration process, because the large centrifugal forces of MAS NMR could lead to a heterogeneous distribution of water and solids in the rotor and consequently the cement hydration might be affected [12]. In contrast, Raman analyses can be carried out under ambient conditions without any spinning. As a result, the wet samples, such as a hydrating cement paste, can be analyzed without being disturbed.

However, in previous studies, bench-mounted Raman spectroscopy is usually employed where the tests can only be carried out in a laboratory condition [20, 21]. In recent years, optical fiber Raman spectroscopy which combines the fingerprint characterization capacity of Raman spectroscopy and the transmission ability of optical fiber, has demonstrated great potential for *on site* real-time monitoring [28-30]. Some pilot studies carried out by the authors have already confirmed the feasibility of establishing and using optical fiber Raman spectroscopy for characterizing some durability-related mechanisms, such as sulfate attack, chloride binding and carbonation attack in cementitious materials [31-33]. Built upon the success of these studies, the feasibility of employing this optical fiber Raman spectroscopy for *in situ* monitoring of ongoing hydration of cement was explored and reported in this paper. It is anticipated that the outcome from this investigation will not only lay a foundation for the development of a novel sensor system to monitor the condition of concrete structure in future, but would also be able to demonstrate its potential for monitoring the hydration process when such kind of information cannot be obtained locally, but essential to know. A good example could be to monitor the cement hydration process when cementitious matrix is used to encapsulate nuclear wastes or even nuclear facilities. For example, in both Chernobyl and Fukushima nuclear disasters, cement-based materials were used to deal with some emergent situations and it would be good to be able to know the on-going reaction remotely so that an optimum formulation could be adopted.

In this paper, an optical fiber excitation Raman spectroscopy which was developed in a previous study was employed to monitor the first 8 hours' hydration [33]. Especially, the hydration of clinker and Portland cement was monitored separately so that the former can be used to follow the evolution of C-S-H gel whilst the latter mainly focuses on the development of AFt and AFm. To verify the information obtained from the optical fiber Raman spectroscopy, bench-mounted Raman spectroscopy、Isothermal Conduction Calorimetry (ICC) and X-ray Diffraction (XRD) analyses were also conducted. Based on the results obtained, the feasibility and potential of the optical fiber excitation Raman spectroscopy as a remote characterizing and monitoring technique for cement hydration is then discussed.

2. MATERIALS AND METHODS

2.1 Materials

The Portland cement and clinker used in this study were supplied by QUINN UK. Their chemical compositions were characterized by X-ray Fluorescence (XRF) spectrometry and are given in Table 1 below. Furthermore, the X-ray Diffraction (XRD) analysis was adopted to complement XRF for further illustrating the phase assemblage of the clinker and cement. Fig.1 presents the XRD diagrams of the clinker and PC used in this study.

2.2 Mix proportion and method

The clinker granules were ground by hand into powder with a fineness of 63 μm. No grinding agent was used in order to avoid introducing any potential fluorescence background. Prior to the Raman and XRD experiments, the pastes were obtained by mixing the clinker/cement powder with deionized water at a water/binder (W/b) ratio of 0.35 by weight, under a controlled temperature of 20(±1) °C. The W/b 0.35 was used to obtain an appropriate workability in terms of mini-slump value (in the range of 55±5 mm).

2.3 Bench-mounted Raman spectroscopy

A bench-mounted Renishaw inVia micro-Raman spectroscopy equipped with a Charged Coupled Device (CCD) detector was applied. The Raman spectrometer is worked under the classical backscattering geometry. To determine the most suitable excitation wavelength, three laser sources with different wavelengths, namely 488 nm, 514.5 nm and 632.8 nm, were compared and the 632.8 nm laser (Helium-neon laser) was considered as the most suitable wavelength in this particular study (detailed information is reported in Section 3.1). The laser beam was focused onto the sample through an M Plan 50X objective with 0.5 N.A. and the laser spot diameter after focus was about 0.8 μm. Measured power at the sampling level was controlled to be about 5 mW in order to avoid the possible thermal effects to the samples which is normally occurred due to excessive heat generated under higher power level. The Raman shift was calibrated before each experiment using the sharp peak of silicon at 520 cm^{-1}. Raman spectra were recorded with an exposure time of 10 seconds and accumulations of 10 in order to improve the signal-to-noise ratio (SNR). The Raman tests were then carried out *in situ* at 45 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 6 hours and 8 hours since the hydration started.

2.4 Optical fiber excitation Raman spectroscopy

A 632.8 nm optical fiber excitation Raman spectroscopy with a configuration of ‘fiber excitation + objective collection’ under a typical 45° optical geometry was employed. Similar to the bench-mounted Raman, this optical fiber set-up allows the measurement of surface micron-area of samples under ambient conditions regardless of analyte states, and only small amount of sample is required, even though compared to the bench-mounted Raman reduced signal level and spectra SNR may be observed due to the lower excitation power density and signal collection efficiency. Further information on this tailor-designed optical pathway can be found in a previous paper by the authors [33]. Similar to the bench-mounted Raman tests, the optical fiber Raman analyses were also carried out *in situ* at 45 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 6 hours and 8 hours since the hydration started.

2.5 X-ray Diffraction (XRD)

In-situ XRD analysis was employed to follow the evolution of the crystalline phases formed during the hydration of clinker and cement. Immediately after mixing the clinker/cement with water, the paste was placed in a sample holder which was then covered with a Kapton foil to avoid moisture evaporation. A PANalytical's XPert Pro MPD diffractometer with an X-ray source of Cu Kα radiation (λ=1.5405 Å) was used to examine the samples in the range of 8° to 45° 2Θ with a step size of 0.02°. The X-ray tube voltage and current were fixed at 40 kV and 40 mA, respectively. The measurement of each diffraction pattern lasts approx. 15 minutes. The evolution of the crystalline phases in the hydrating paste were then analyzed *in-situ* over time at 45 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 6 hours and 8 hours. The identical parameters were adopted to analyze the clinker and cement in the 2Θ range of 5° to 65°. The obtained XRD patterns were then processed using the X'Pert Highscore Plus (PANalytical) software.

2.6 Isothermal Conduction Calorimetry (ICC)

Isothermal Conduction Calorimetry (ICC) analysis was conducted to monitor the evolution of heat and the production rate of heat during the hydration process of the paste. Using this information, the hydration process could then be followed. In this study, the test was carried out in a TAM Air Calorimeter using an internal mixing method where the clinker/cement powder was internally mixed with water at a water/solid ratio of 0.35. The calorimeter cell was kept at a constant test temperature of 20(±0.1) °C. The rate and the total amount of heat evolution from the early stage was recorded.

3. RESULTS AND DISCUSSION

3.1 Selection of an appropriate excitation laser wavelength

The excitation laser wavelength is the most important and crucial factor for avoiding the occurrence of the troublesome fluorescence which could impose strong disturbance to or even totally hamper the intrinsically weak genuine Raman peaks [34, 35]. This is, in particular, the case when cementitious materials are to be characterized by Raman spectroscopy [34, 36]. Since the occurrence of the fluorescence is directly related to the laser wavelength used to interrogate the samples, the selection of a suitable laser wavelength is, thus, essential. Based on an extensive literature review, three most widely used laser wavelengths were identified to be potentially suitable for characterizing cement and concrete, namely, 488nm, 514.5nm and 632.8nm. These three laser wavelengths (with the established laser power and accumulation) were then employed to characterize clinker in order to establish the most suitable wavelength to be used in this study. Only clinker was used for this purpose because the fluorescence that could be generated from the grinding agent or grinding process in the PC could potentially complicate the wavelength selection process [36]. The Raman spectra of the clinker obtained from each wavelength are presented in Fig. 2 below.

Figure 2 shows the Raman spectra of the clinker analyzed under three different wavelengths, viz. 488nm, 514.5nm and 632.8nm, respectively. Obviously, all three lasers can be applied to effectively characterize the clinker phases. More importantly, the Raman spectrum collected under the longest excitation wavelength of 632.8nm showed relatively low background as well as better image quality (especially, in terms of the intensity of signal). Hence, the 632.8nm laser was selected as the most suitable excitation wavelength in this particular case, and the Raman bands assignment is thus only given below to the spectrum obtained at this particular wavelength (i.e. Fig. 2c) as the Raman shifts are independent of the wavelength. In Fig. 2c, the band in 800 - 900 cm^{-1} represented the ν_1 (SiO_4) Si-O symmetrical stretching

(SS) vibrations in the calcium silicates (i.e. C_3S and C_2S). The sharp and intense peak at about 829 cm^{-1} could be assigned to the Si-O SS (ν_1) vibrations of C_3S, and a shoulder at 857 cm^{-1} was from the Si-O SS vibrations of the C_3S and C_2S phases. The band observed at about 888 cm^{-1} could be a satellite of the vibrations of C_3S and C_2S [20, 21]. It can be seen from Fig. 2c that these three bands dominate the spectrum which corresponds well with the fact that C_3S and C_2S phases are the primary constituents of the clinker, i.e. about 65~85%. Besides, a hump was visible in the range of 600 – 750 cm^{-1} which could be associated with the ν_3 AlO_4 vibration of C_3A and ν_1 $[(Fe,Al)O_4]/[(Fe,Al)O_6]$ vibration of C_4AF phases in the clinker [18, 24]. In addition, several humps were also identified which could be attributed to the Ca-O vibrations (200-450 cm^{-1}) and the O-Si-O bending modes (510-580 cm^{-1}) [20, 21].

3.2 *In situ* monitoring of clinker hydration with Raman spectroscopy (with/without optical fiber)

As discussed in Section 1, the hydration of clinker and cement could generate different hydration products owing to the absence or presence of gypsum. The hydration of clinker minerals mainly yields C-S-H, CH and C-A-H, while the hydration of cement is accompanied by the formation of not only C-S-H and CH, but also sulfate-bearing phases, i.e. AFt and AFm. Therefore, similar to the approaches adopted by most of the researchers when the hydration is investigated, in the current study, to clearly illustrate the hydration mechanisms and kinetics of cement and also to demonstrate the feasibility of characterizing on-going hydration with optical fiber excitation Raman spectroscopy, the first 8 hours' on-going hydration of clinker and cement were monitored separately, by bench-mounted Raman and fiber excitation Raman spectrometers respectively.

Furthermore, to monitor the evolution of the reaction products, a selected area needs to be monitored *in situ* continuously over time. Since the hydration of PC is mainly dominated by two hydrate systems, viz. C_3S/C_2S-H_2O system to yield C-S-H and CH, and C_3A/C_4AF-$C\check{S}$-H_2O to yield AFm/AFt [3], different focuses have been given to the clinker and the PC respectively as follows, so that the full picture of PC hydration can be clearly identified and followed:

(i) For clinker hydration, C-S-H was selected as the main hydration product to be continuously monitored over time. As elaborated before, another advantage of using clinker, instead of PC, is that the fluorescence that could be generated from the grinding agent or grinding process in the PC can be effectively avoided (it should be noted that the clinker used in this study was ground in the laboratory without using any grinding agent). In this way, the features associated with the hydration products can be well characterized and this information can, in turn, be used as benchmark for future Raman analysis.

Additionally, the reason that CH was not considered as a target hydration product in this study is because the hydration process was monitored by Raman spectroscopy from around 45 minutes onwards. At this very early stage, it is difficult to identify CH because its precipitation is normally expected towards the end of induction period [1-3].

(ii) For cement hydration, sulfate-bearing phases (i.e. AFt and AFm) were selected as the main hydration product to be continuously monitored over time.

It is anticipated that by combining the information obtained from the above two aspects, the capability of Raman spectroscopy, in particular, the optical fiber Raman spectroscopy for monitoring the evolution of PC hydration can be clearly demonstrated.

3.2.1 Bench-mounted Raman spectroscopy analysis

In the current study, the first 8 hours' hydration of PC clinker was investigated *in situ* by Raman spectroscopy, covering the three most crucial hydration stages namely pre-induction, induction and acceleration periods. Figure 3 presents the Raman spectra of the first 8 hours hydration of clinker at certain time intervals. The Raman bands and related assignments are summarized in Table 2. As shown in Fig. 3, compared to the spectrum of the raw clinker which was dominated by a sharp and well-defined band centered at about 829 cm^{-1} (C_3S/ C_2S), the Raman spectra of the hydrated paste between 45 minutes and 2 hours showed much different pattern, with a quite weak and featureless hump emerging in the range of 800 – 870 cm^{-1}. This hump, emerged probably even earlier than 45 minutes, could have come from the ν_1 symmetrical stretching (SS) vibrations of the Q^0 monomeric silicate units (marked as Q^0 (m_1) in Fig. 3 to differentiate it from other Q^0 units) [17], viz. the intermediate phase (*product B*) in the formed protective surface layer surrounding the clinker grain [2, 11, 37]. This intermediate phase is metastable respect to the C-S-H and will finally transform to the more stable C-S-H [38]. The quite weak intensity nature of this hump could be owing to the altered structure of these Q^0 monomers, as it has been reported that these intermediate Q^0 species are probably attached by hydrogen atoms, which are structurally distinct from the anhydrous C_3S and C–S–H phase [9, 11]. Noteworthy, in the current study, it is the thin layer formed by this intermediate phase on the clinker surface was analyzed, because Raman spectroscopy is a surface sensitive technique. What's more, the laser penetration depth of the Raman analyses in the current study might have been further reduced since the clinker is in dark grey color which could adsorb some of the illuminating laser. The identification of the intermediate phase formed in the clinker grain indicates that the induction period (approx. within 3 hours) can be well identified by Raman spectroscopy.

From 3 hours' hydration onwards, marked changes in the Raman spectra were clearly seen, probably due to the dissolution and phase transformation of the intermediate phase and breakdown of the protective coverage. There were intense bands emerged at about 800 – 870 cm^{-1}, encompasses several distinguishable peaks. The peak centered at about 829 cm^{-1}, could be ascribed to the ν_1 SS vibrations of the Q^0 silicate monomers of the unreacted C_3S/C_2S [17]. This peak, which was disappeared between 45 minutes and 2 hours, but emerged again, could be due to the rupture of the initially formed protective barrier and hence, become detectable again after the anhydrous clinker was re-exposed to the illuminating laser. What's more, this peak decreased with time, which correlates well with the consumption of C_3S/C_2S by ongoing hydration. The other two peaks, centered at about 836 cm^{-1} and 854 cm^{-1}, could be allocated to the Q^0 monomeric units while the slow transformation from Q^0 to more stable C-S-H is initiated after the completion of induction. As these Q^0 species could be structurally different from the Q^0 (m_1) formed in the induction period, they have been labeled as Q^0 (m_2) in Fig. 3. During the meantime, a weak band also can be observed in 870 – 900 cm^{-1}, which corresponds to the formation of Q^1 dimers (ν_1 SS vibrations) [17]. This could have been caused by the polymerization/oligomerization of silicate monomers during the acceleration period [9]. These much-altered distinct Raman features after 3-hour hydration, viz. the appearance of the Q^0 and Q^1 bands, can be used to clearly indicate the onset of acceleration period and the termination of induction stage. This again showed the unique strength of Raman spectroscopy for characterizing the hydration process of cement.

Hence, thanks to the surface inspection of the Raman spectroscopy, the progress of clinker hydration in terms of the formation of the intermediate Q^0 monomers and the later polymerized long silicate units (Q^1) can be well recognized, with both the induction and onset of acceleration period being clearly differentiated. It is thus the authors' view that the results obtained can fully justify the capacity of Raman spectroscopy for investigating the hydration of clinker minerals. Furthermore, as highlighted before, Raman spectroscopy can be undertaken without any disturbance to the status of the wet sample which is also an obvious advantage over MAS NMR. Therefore, Raman spectroscopy can be considered as an invaluable complement to NMR for studying cement hydration.

Apart from the bands in 800 – 900 cm^{-1} associated with the silicates and initial hydrates, trace of sulfate phases were also identified at about 978 cm^{-1} (ν_1 SO_4), 628 cm^{-1} (ν_4 SO_4), 457 cm^{-1} (ν_2 SO_4) and 1143 cm^{-1} (ν_3 SO_4) respectively [39]. The occurrence of these sulfate-bearing phases could be attributed to the contamination by sulfates. Additionally, the bands emerged at 1068 cm^{-1} from 3 hours onwards could be assigned to the ν_1 CO_3 of calcium carbonates [40], which might have been caused by the carbonation during sample preparation. Compared to the ν_1 CO_3 band of the crystallized carbonates showing well-resolved sharp peak at 1085 cm^{-1}, the carbonates formed here could be amorphous phase as manifested by the red-shifted (lower frequency) frequency and much broader band shape than crystalline polymorphs.

3.2.2 Optical fiber Raman spectroscopy analysis

Figure 4 shows the Raman spectra of the hydration of clinker retrieved under optical fiber excitation Raman spectroscopy. The Raman bands and assignments are summarized in Table 3. For the hydration between 45 minutes and 2 hours, a weak hump can be observed at 800 – 870 cm^{-1}, which could be attributed to the SS vibrations of the intermediate Q^0 monomeric silicate units ($Q^0 (m_1)$) [17]. From 3 hours' hydration onwards, a relatively intense band can be seen in 800 – 900 cm^{-1}. This band could be contributed by the Q^0 monomers of the C_3S/C_2S, the $Q^0(m_2)$ species undergoing transformation, as well as the Q^1 silicate dimers [17]. The recognization of the Q^1 units marks the polymerization of silicate monomers hence the onset of acceleration period. On the other hand, the Raman features of the AFm due to contamination were recognized as well, at 982 cm^{-1} (ν_1 SO_4), 453 cm^{-1} (ν_2 SO_4) and 620 cm^{-1} (ν_4 SO_4) respectively [39]. Obviously, the general pattern of the Raman spectra obtained from optical fiber Raman path is similar to that observed in the bench-mounted Raman system. Hence, from the above results, it can be concluded that optical fiber excitation Raman spectroscopy is adequate to monitor the ongoing hydration of clinker *in situ*.

However, by comparing Fig. 3 and Fig. 4, it becomes obvious that the signal of the spectra obtained under fiber excitation Raman was much weaker than that of bench-mounted Raman system. This could be primarily caused by the lower laser-power density hence reduced excitation efficiency of optical fiber excitation Raman system owing to its much larger excitation spot area on the sample. In addition, the lower signal collection efficiency under optical fiber excitation Raman spectroscopy could make contributions as well. The bench-mounted Raman spectroscopy was configured on backscattering geometry, which can maximize the overlapping between the excitation light-cone and the signal-cone, leading to much improved signal collection efficiency. However, under the optical fiber excitation Raman spectrometer, the signal was collected at 45° configuration which would reduce the signal collection efficiency owing to the decreased overlapping of the laser-cone and the signal cone [27, 41].

3.2.3 X-ray Diffraction (XRD) analysis

In this study, XRD analysis was conducted to provide some supplementary information to support the Raman analysis. Figure 5 is the XRD patterns of the first 8 hours' on-going hydration of clinker. As can be seen from Fig. 5, the anhydrous mineral phases, i.e. C_3S, C_2S, C_3A and C_4AF, were clearly identified. Obviously, the peaks of these clinker minerals, especially the peaks associated with the primary calcium silicates (C_3S and C_2S), steadily decreased over 8 hours, indicating the consumption of these silicates during the hydration process. On the other hand, at 2 hours, a peak appeared at 18° 2θ, which corresponds to the Portlandite. This peak, since hydration of 3 hours, increased sharply with time, indicating the rapid formation of Portlandite hence onset of acceleration period, which is in good agreement with the Raman spectroscopic results discussed in Section 3.2.1. The existence of C-S-H was not characterized because of its poorly-ordered structures. However, the formation of C-S-H can be indirectly verified by the consumption of calcium silicates (C_3S and C_2S) and continuous formation of the Portlandite.

3.2.4 Isothermal Conduction Calorimetry (ICC) analysis

Furthermore, ICC analysis was carried out to collect some information on the kinetics of the hydration of clinker in order to verify the results obtained from Raman analysis. The rate of heat evolution curve is shown in Fig. 6, with an inset of rescaled axes added to get a clear view of the main hydration peak, and the critical times (i.e. 45 minutes, 3 hours and 8 hours) at which the Raman and XRD tests were carried out was clearly marked in an attempt to correlate the ICC results with both the Raman and XRD results. Besides, the total heat liberation is also shown in Fig. 7. In Fig. 6, an instant exothermic peak can be noticed immediately after mixing. This peak at the pre-induction period indicates an initial burst of heat, which could be mainly attributed to the wetting of clinker, the rapid dissolution of the interstitial phases in clinker (namely aluminates, alkaline sulfates and free lime), as well as the superficial hydration of C_3S phase [3, 42]. Followed by this, the heat curve declined to an induction period which lasted for a few hours (approx. 2-3 hours). This period indicates clearly the slowdown of heat release due to the slow activity of the system. This is probably owing to the precipitation of early hydration products (e.g. intermediate phase Q^0 units) and thus an initial coating on the mineral surfaces, hindering further hydration of the clinker [3, 11]. In Figs. 3 and 4, the Raman characterization was undertaken at 45 minutes, 1 hour and 2 hours which were within this induction period, hence the weak bands exhibited during this period is in good agreement with these ICC features. Meanwhile, the XRD figures obtained within 3 hours also showed similar patterns. This period was then followed by an acceleration period (shown in the figure as a rising curve to form a ‘major peak’) during which the intermediate phase transformed and C_3S consumed rapidly to form considerable amount of C-S-H (e.g. Q^1) and Portlandite [3]. Hence, the Raman results as discussed above with the emergence of polymerized hydration products (e.g. Q^1) from 3 hours onwards are well verified by this phenomenon, which also corresponds well with the XRD patterns. The total heat evolution, as shown in Fig. 7, increased over time, indicating the continuous hydration reactions.

3.3 *In situ* monitoring of Portland cement hydration with Raman spectroscopy (with/without optical fiber)

3.3.1 Bench-mounted Raman spectroscopy analysis

From the results presented in Section 3.2, the optical fiber excitation Raman spectroscopy showed good potential for tracing the evolution of C-S-H during the first 8 hours' hydration of clinker, even though the Raman signal under the fiber excitation mode was less stronger. As explained before, in this section, the main focus was to monitor the evolution of sulfate-bearing phases (i.e. AFt and AFm) formed during the PC hydration continuously over time so that the capacity of the optical fiber Raman spectroscopy for monitoring the hydration process can be verified fully. Hence, during the experiment, a sampling point with some distinct features of AFt/AFm phases was first selected which was then monitored continuously over time. The Raman spectra thus obtained under bench-mounted Raman and optical fiber excitation Raman spectrometers are presented in Fig. 8 and Fig. 9 respectively. The Raman bands and related assignments are summarized in Table 4 and Table 5 respectively.

As shown in Fig. 8, the sulfate-bearing phases (AFt & AFm) were formed immediately upon hydration, and the following features can be observed:

(i) In the spectra from 45 minutes onwards, there were two well-defined peaks located at 983 cm^{-1} and 991 cm^{-1} respectively, which could be attributed to the ν_1 SO_4 symmetrical stretching (SS) vibrations of AFm and AFt, respectively. At the same time, the other three SO_4 internal vibration bands of AFt/AFm, i.e. 452 cm^{-1} (ν_2 SO_4 symmetrical bending (SB)), 620/628 cm^{-1} (ν_4 SO_4 antisymmetrical bending (aSB)) and 1107 cm^{-1} (ν_3 SO_4 antisymmetrical stretching (aSS)), were also observed [18, 19, 39]. The above Raman features can be well corroborated by the well-established theory that AFt/AFm is formed immediately upon the hydrations between the C_3A or C_4AF phases, calcium sulfate and water [1-3];

(ii) In addition, within the hydration of 2 hours, the intensity of the SO_4 symmetric stretching peak of the AFm phase was relatively higher than that of AFt phase. However, these features altered from 3 hours onwards with the ν_1 SO_4 SS peak of AFm decreased and AFt increased, forming a doublet-like shape. In the literature, it has been reported that, during early stage of hydration, AFm and AFt phases could co-exist and, depending on the availability of the dissolved sulfate ions, AFm could even dominate [43]. Nonetheless, with the increase of the availability of the sulfate ions, it has been confirmed that the ratio between AFm and AFt could change, with AFt gradually dominating the sulfate-bearing phases formed during the early stage of hydration [3]. It is encouraging to see that the above very delicate features of the evolution of sulfate-bearing phases, which is often difficult to be recognized by other techniques, have been nicely identified by the Raman spectroscopy which clearly demonstrated the great potential of monitoring the hydration of cement with the sophisticated characterization capacity of Raman spectroscopy.

The shoulder appeared at 1004 cm^{-1} which decreased with time, and the unchanged weak band at 1143cm^{-1}, should be assigned to the ν_1 SO_4 SS and ν_3 SO_4 aSS vibrations of gypsum respectively [19, 44]. The weak band appeared at 1083 cm^{-1} should be ascribed to the symmetrical stretching of CO_3 in the carbonates formed during the sample preparation [31, 32, 40, 45, 46]. Hence, Raman spectroscopy shows superiority for monitor the evolution of sulfate-bearing phases in the hydrated cement paste.

3.3.2 Optical fiber Raman spectroscopy analysis

The Raman spectra of the first 8 hours ongoing hydration of cement under optical fiber excitation Raman spectroscopy are shown in Fig 9. Table 5 presents the related Raman bands and assignments. By comparing Fig. 8 and Fig. 9, it is apparent that the Raman spectra of cement hydration under optical fiber excitation mode showed extremely similar features as those under bench-mounted Raman spectroscopy. As can be seen from Fig. 9, the distinct peaks, viz. 982 and 991 cm^{-1}, appeared immediately after hydration which has dominated the whole initial 8 hours hydration, should be attributed to the ν_1 SO_4 SS of AFm and AFt respectively. In addition, a peak appeared at 453 cm^{-1} (ν_2 SO_4 SB), a doublet at 620/626 cm^{-1} (ν_4 SO_4 aSB) and a hump emerged at 1106 cm^{-1} (ν_3 SO_4 aSS) could be assigned to the formation of AFt/AFm phases as well [18, 19, 39]. At the same time, the weak band located at 1144 cm^{-1} should be from the ν_3 SO_4 aSS of gypsum [19, 44]. The trace quantity of calcium carbonate was also detected by optical fiber Raman, with the weak band at 1082 cm^{-1} (ν_1 CO_3 symmetric stretching) [31, 32, 40, 45, 46], illustrating the high sensitivity of this optical fiber-based Raman monitoring system. Based on our results, it can be concluded that although the Raman signal under fiber mode was relatively lower, optical fiber excitation Raman spectroscopy has demonstrated its great potential for continuously tracing the evolution of cement hydration process.

3.3.3 X-ray Diffraction (XRD) analysis

The supplementary XRD analysis on the cement hydration is shown in Fig. 10. It can be seen that the AFt and AFm formed immediately after hydration, which well supports the findings from the Raman characterization results in Figs. 8 and 9. In addition, their peak intensities were increasing with the ongoing hydration, indicating the continuous formation of these sulfate-bearing phases. It should be noted that both AFt and AFm peaks have been clearly identified from 45 minutes onwards, which again confirmed the findings from the Raman analysis showing the co-existence of these two crystals. The peaks between ~28 and ~35° 2θ, which corresponds mainly to the anhydrous C_3S and C_2S phases, decreased with time. This indicates the consumption of these silicate minerals over time. At the same time, the C_3A and C_4AF were also identified in this area. Besides, it can be noticed that the three peaks of gypsum exhibited within 6 hours but disappeared in the 8 hours' diagram, indicating the consumption of almost all of the gypsum after 8 hours hydration. This feature, again, correlates well with the Raman results. On the other hand, there was no significant formation of Portlandite before 3 hours, but became significant at 8 hours, which is in good agreement with the ICC results presented below. As clearly showed in the ICC results (Fig. 11), the period between 6 and 8 hours is the main acceleration stage and the rapid formation of C-S-H and Portlandite is to be expected [3, 42].

3.3.4 Isothermal Conduction Calorimetry (ICC) analysis

The ICC result is shown in Fig. 11 (rate of heat evolution) and Fig. 12 (total heat) respectively. Evidently, the rate of heat evolution curve of cement showed most of the patterns to be anticipated from the hydration of a typical Portland cement, which obviously differs from that of the clinker (Fig. 6). It can be seen that, there was an immediate exothermic peak just after mixing. In addition to the factors which contributed to the similar exothermic peak in clinker, the immediate formation of the sulfate-bearing phases, viz. AFt and AFm, from the reactions between aluminates/aluminoferrites and calcium sulfate should also contribute to this strong exothermic peak here [3]. This has also been well evidenced by the 45 minutes' Raman results (as presented in Figs. 8 and 9) as well as the XRD patterns (Fig. 10). After this initial fast reaction, a short induction period appeared mainly attributed to the nucleation of the superficial C-S-H formed at the early stage. Followed by this, the curve rose up from approx. 3 hours, indicating the start of the acceleration period from the rapid hydration of C_3S to form C-S-H and Portlandite. After that, the rate of heat evolution slowed down gradually.

4. CONCLUSIONS

The successful application of optical fiber Raman spectroscopy in biomedical and chemistry areas inspires us its potential in monitoring cement hydration. In the current study, a tailored optical fiber excitation Raman spectroscopy was developed and applied for *in situ* monitoring of the first 8 hours hydration of clinker and cement. Under excitation wavelength of 632.8 nm, the evolution of hydrated phases, i.e. C-S-H in clinker hydration and AFt & AFm in cement hydration, have been successfully traced by optical fiber excitation Raman spectroscopy, which clearly demonstrated its great potential in future civil engineering applications. Additionally, its surface sensitive nature has also made it uniquely placed for characterizing the early hydration process of cement. However, the Raman spectra under optical fiber excitation mode showed weak signal. This, together with its potential to quantify the hydration products formed needs to be further studied in the future.

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