1 **Monitoring hydration of UHPC and conventional paste by**
2 **quantitative analysis on Raman patterns**

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Abstract

Cement hydration governs physical, chemical and mechanical properties of cement pastes. Therefore, tracing hydration progress in different types of cement pastes can help to understand different hydration mechanisms and paste behaviours. In the present research, a quantitative analysis on Raman spectroscopy (RS) patterns for conventional cement paste and ultra-high performance concrete (UHPC) matrix at different hydration ages has been applied. It has been found that quantitative analysis on peak area of Raman patterns is fully capable to differentiate between conventional cement hydration and pozzolanic reaction in UHPC. The result also showed that silica fume included in the UHPC matrix was more reactive at early ages, which was completely in agreement with reduction of calcium hydroxide (CH) content at the same hydration period.

Keywords: Raman Spectroscopy; quantitative analysis; cement hydration; pozzolanic reaction; UHPC

1. Introduction

Hydration is the chemical reaction between cement and water, which results in the physical change of the cement paste from a liquid to a solid. Cement hydration process has direct effects on physical, chemical and mechanical properties of cement pastes, such as setting time, viscosity, compressive strength, etc. Therefore, understanding the hydration mechanism in cement paste can provide a good foundation of monitoring and assessing cement pastes behaviours.

To understand the hydration mechanism, researchers have used different methods, e.g. calorimetric methods, Scanning Electron Microscopy (SEM), X-Ray Diffraction, and Infrared Spectroscopy (IR), to monitor hydration heat or phase development in the microstructure [1-4]. Although these methods are powerful to monitor the hydration

progress, they either measure hydration indirectly or require complicated and time-consuming sample preparation processes. For example, if SEM is used to look at the microstructure of a cement paste, the free water in the paste needs to be replaced with isopropanol to stop hydration, and then the sample needs to be dried in an oven. The whole procedure can take up to one week especially for large and old samples [5,6]. In addition, the prepared samples can only be used once, which makes it almost impossible to continuously monitor the hydration process of the paste.

Recently research on Raman spectroscopy (RS) shows this technology has great potential to investigate the real-time hydration process in cement paste. RS is a vibrational spectroscopy method that is capable of identifying different chemical composition within a sample [7]. In this method, the sample surface is illuminated with a laser beam. The interaction between molecule bonds and laser photons results in a shift in photons energy level [8]. Since these energy shifts are unique for each different molecular bond, RS can be used to identify different chemical composition in a composite. Water has a weak Raman scattering, which does not interfere with the shifts of other components in the water [9]. Therefore, RS is applicable to fresh cement paste, and no sophisticated sample preparation is needed. This allows continuous in-situ observation of cement hydration.

For cement application, Bensted and his co-workers [8, 10] firstly used RS to identify main shifts of different synthetic clinker phases. Other researchers then identified characteristic Raman shifts for different cement ingredients, hydration products, and gypsum phases [11-15]. A recent research reported by Garg et al. [12] showed that RS could be successfully used to study hydration process of Portland cement pastes at

different ages. Liu et al. [14] expanded the application of RS to continuously observe the hydration process of Portland cement pastes with different water-to-cement ratios (w/c ratios) during setting period.

Besides its application in the clinker phases and cements, RS has also been used to characterize various supplementary cementitious materials, including fly ash, slag, and metakaolin [16-18]. A variety of crystalline and glassy mineral phases were detected in the fly ash. These were elemental carbon, quartz, anhydrite, C_3S , and calcium aluminate glass, among others [16]. The main compounds detected in slag by RS included the pure graphite carbon, iron compounds, and calcium silicates [16]. Different from fly ash and slag, when RS was applied to characterize metakaolin, the spectrum only showed a broad band with a small peak for the water molecule contained in the metakaolin, and it was not possible to identify other phases [17,18]. When integrating these supplementary cementitious materials into cement paste, the pozzolanic reaction will occur with the calcium hydroxide formed from cement hydration, which can also be tracked by Raman spectroscopy. Garg et al. used RS to chemically map the intensity and spatial distribution of calcium hydroxide for studying the pozzolanic reaction of three different types of fly ash. From the chemical maps, they found that the pozzolanic reaction led to the decline of both CH intensity and content in the paste [12]. A study on the reaction kinetics in blended white cement pastes containing metakaolin by using Raman spectroscopy was also implemented by Frias and Martinez-Ramirez [18]. RS was able to detect the hydrated phases (C_2ASH_8 and C_3ASH_6) formed from the white cement-MK hydration reaction. From these studies, it can be seen that RS are efficient in observing pozzolanic

99 reactions either by tracking the content of CH or the detection of newly formed hydrated
100 phases.

101 This paper focuses on monitoring hydration processes in different cement pastes by
102 applying quantitative analysis with Raman spectroscopy. Two different types of cement
103 pastes are studied: conventional cement paste that consists of ordinary type I Portland
104 cement and a type of Ultra-High Performance Concrete (UHPC) matrix that consists of
105 Class H oil well cement, silica sand, silica flour and silica fume. UHPC is a cementitious
106 composite material with water to cementitious materials ratio of less than 0.25 and
107 compressive strength of higher than 150 MPa. It shows remarkable mechanical and
108 durability properties and its microstructure differs significantly from conventional or high
109 performance concrete (HPC) [19, 20]. Due to low w/c ratio of UHPC, usually cements
110 with moderate fineness and low C₃A content like class H oil well cement (OWC), which
111 have lower specific surface area than ordinary Portland cement, are used to improve the
112 flowability [21]. Also, high proportion of silica fume and other siliceous materials are
113 added in UHPC mix design to improve strength and mechanical properties by their strong
114 pozzolanicity [22, 23].

115 The Raman patterns obtained from each cement paste at different ages (3, 7, 14, 21,
116 and 28 days after casting) were analysed in this study. The research shows that RS is a
117 powerful tool that can help to chase the hydration progress caused by different hydration
118 mechanism, i.e. conventional hydration and pozzolanic reaction.

2. Materials and Experiments

2.1 Raw materials

Ordinary Type I Portland cement was used to mix conventional cement paste. The mean size of cement particles was 13 μm , determined through a laser particle size analyzer. The Blaine surface area was 400.8 m^2/kg . The chemical composition of this type I cement was measured with XRF and it is listed in Table 1.

Table 1: Chemical compositions of raw materials

Compound (%)	Type I	Class H	Silica sand	Silica flour	Silica fume
SiO ₂	20.49	21.75	99.20	98.87	93.00
Al ₂ O ₃	4.56	2.73	0.07	0.25	0.59
Fe ₂ O ₃	2.82	4.43	0.05	0.03	0.73
CaO	64.88	64.25	0.17	0.19	1.29
MgO	2.57	2.35	0.06	-	0.17
SO ₃	3.17	2.85	0.01	0.02	0.13
Na ₂ O	0.16	0.09	-	-	-
K ₂ O	0.39	0.17	-	0.01	0.02
Na ₂ O _{eq}	0.42	0.20	-	-	-
LOI	1.20	-	-	-	-

For the UHPC paste, Class H cement (oil well cement specified by American Petroleum Institute (API)), processed fine silica sand, finely ground silica flour, and micro silica fume were used. The mean sizes of the particles were 20 μm for class H cement, 313 μm for silica sand, 18 μm for silica flour and 6 μm for silica fume, determined through a laser particle size analyser. The chemical compositions for these

materials are also listed in Table 1. The mineral compositions for both type I and class H cements are listed in Table 2. These compositions were calculated based on the Bogue's equation [24].

Table 2: Mineral compositions of Type I Portland cement and class H cement

Compound	Wight, %	
	Type I	Class H
C_3S	64.88	63.24
C_2S	20.49	14.65
C_3A	4.56	N/A
C_4AF	2.82	13.27

2.2 Sample preparations

For conventional paste, water-to-cement ratio of 0.6 was used. The paste was properly hand mixed for 5 minutes and transferred to the standard tissue culture dishes (cylindrical plastic sample holders) with a diameter of 50 mm and depth of 10 mm. After transferring the paste, the sample holder was then slightly tapped to consolidate the paste, and the specimen would be ready to be studied with RS. Including mixing, the whole sample preparation procedure took around only 6-7 minutes. Compared to the traditional SEM and XRD, the sample preparation for RS was much simpler.

The mix proportion of the UHPC is listed in Table 3. For UHPC matrix, firstly the four constituent materials were dry mixed for about 5 minutes. Then, water and superplasticizer were combined before being gradually added to the dry mixture while actively mixing. Mixing time was approximately 15 minutes to achieve a wet, flowable matrix. When mixing was done, similar to conventional cement paste, UHPC matrix was

transferred to the standard tissue culture dish and slightly tapped to give a relatively smooth surface [25].

Table 3: UHPC mix composition [25]

Materials	Proportion by weight
Cement	1.00
Silica Sand	0.967
Silica Flour	0.277
Silica Fume	0.389
Superplasticizer	0.0171
Water (tap)	0.208

For both pastes, 3 replicas were used. All of the specimens were cured under sealed condition in a laboratory with controlled temperature of 22 °C throughout the measuring window.

2.3 Raman measurements

The Raman system used was a Renishaw Invia micro-Raman spectrometer with a CCD detector. Samples were illuminated with a 633 nm He-Ne Laser (Renishaw RL 633 laser). The laser power was about 4 mW on the surface of the sample. During each test, scanning was carried out by using the syncro mode from 300 to 2000 cm⁻¹. The exposure time for each scan was 10 seconds and it took 40 to 60 seconds to acquire one spectrum. All the spectra were obtained with a 50× magnification objective. The laser spot had a diameter of 4 μm with this magnification. Before each test, calibrations were done by utilizing the 520.5 cm⁻¹ line of a silicon wafer. Data acquisitions were carried out with the WiRE3.3 software (Renishaw, Illinois).

During the study, Raman spectra for each raw material (powders) were obtained first. RS analysis was applied at 15 random locations and the averages of these 15 spectra were

taken as the RS spectrum for each powder that was used. For the studied pastes, before each Raman test, all of the samples surfaces were sanded and cleaned with compressed air. This helps to improve the representation of the specimen. Then, 10 discrete points were picked randomly for each sample and the average of the total 30 spectra for each age (with 3 replicas) were used. All of the raw spectra that obtained were processed with background correction to further assist quantitative analysis.

3. Results and discussions

3.1 Raman spectra for raw materials

The Raman patterns for each raw material (powder) were obtained to assign the characteristic Raman shifts for each material. These assigned Raman shifts were later used as references to identify each individual component in hydration process at different ages. The Raman patterns for Type I Portland and class H cements are shown in Figure 1. The phases for both cements were identified based on findings of pioneer researches [8, 26-28]. It can be seen in the figure that the peaks for C3S, C2S, and gypsum can be identified clearly in both cements, which are at the Raman shift of 833, 887 and 1005 cm⁻¹, respectively. However, the peak intensity of gypsum is higher in class H cement than that in Type I Portland cement. The most remarkable difference between two Raman patterns lies in the identification of C3A peak. In pattern for Type I cement, C3A peak can be easily identified at Raman shift of 552 cm⁻¹. While in pattern for class H cement, due to overlap with shift range of C4AF, the peak for C3A cannot be detected. This is in accordance with the XRF result (Table 2). The lower content of C3A in Class H cement

194 than Type I Portland cement generates weaker peak that is easily to be obscured by that
 195 of C4AF.

Figure 1. Raman spectra for type I and class H cements

198 Apart from class H cement, three silica components were also included in UHPC
 199 matrix. As it is seen in Table 1, all silica phases are primarily composed of silicon
 200 dioxide (SiO_2). However, due to the differences in their molecular structures, they can
 201 still be distinguished according to their individual spectral features. Raman patterns for
 202 silica flour, silica sand, and silica fume are shown in Figure 2. It is observed that Raman
 203 pattern for silica fume has a unique, strong peak at 517 cm^{-1} , which can be taken as its
 204 characteristic peak. Also, it can be seen that both silica flour and silica sand have a strong
 205 peak at Raman shift of 465 cm^{-1} , while silica flour has other two strong peaks at 1371 and
 206 1397 cm^{-1} . These two strong peaks are not found in the spectrums of neither silica sand
 207 nor silica fume; thus, they can be taken as the characteristic peaks for silica flour.

Figure 2. Raman spectra for silica components in UHPC: (a) silica flour; (b) silica sand; (c) silica fume

3.2 UHPC Matrix

Raman patterns for UHPC matrix were obtained at different ages after casting (3, 7, 14, 21 and 28 days). The pattern for hydrated UHPC matrix at 3 days is shown in Figure 3. It is observed that characteristic peaks for class H cement components and silica phases can be found easily. These included calcium silicates (C_3S & C_2S), and all three silicas. It can be seen that the peak for silica fume has the highest intensity. This can be due to the fact that the vibration of silica fume molecule is more sensitive to used laser (633 nm). Figure 3 also clearly shows peaks for the two hydration products, ettringite (AFt) and calcium hydroxide (CH). The identification of these two ingredients was based on previous studies of sulfate phases in cement [11-13] and measurements on pure CH crystals [14,29]. It also needs to be mentioned that another hydration product, C-S-H gel,

did not give consistently detectable Raman peaks under the experimental condition used. During the measurements, the peak for C-S-H gel was only detected occasionally at some locations instead of all the measured points, and the peak intensity of the C-S-H gel was much weaker than other compounds in the paste. After being averaged, the C-S-H peak was almost invisible from the patterns. The similar phenomena also occurred in the previous researches [17,18], which should be attributed to the poor crystallinity of C-S-H gel [10].

Figure 3. Raman spectra for UHPC matrix at the age of 3 days

To chase the hydration progress in UHPC, RS patterns at different hydration ages are stacked and depicted in Figure 4. It is clear from the patterns that the peaks found for UHPC in Figure 3 are consistently present at all hydration ages. Due to high intensity and predomination of silica fume peak over other UHPC components, monitoring the changes in peak intensity of other components was not visually possible. Therefore, a quantitative analysis on peak area was applied on UHPC to investigate the evolution of the components at different hydration ages.

Midpoint Riemann sum approximation was used in order to calculate the peak areas. For that purpose, the designated area under specific peak was divided into many small rectangles with thickness of roughly 0.8 cm^{-1} . Then, the area of each small rectangle was calculated. Adding the area of all these small rectangles together, gave a good approximation of the peak area.

Figure 4. Stacked spectra for UHPC at the hydration ages from 3 to 28 days

It is known that amongst the three silicas used in UHPC matrix, only silica fume can react with calcium hydroxide (CH) in the presence of water during hydration [30]. Both silica sand and silica flour perform as fillers and do not react in hydration process. Thus, the area under characteristic peaks of these two components is assumed to be constant at different hydration ages. This constant area can be used as reference to track the changes of other components of UHPC at different ages. The peak area ratio of each component over that of both the silica flour and the silica sand was traced. Thereafter, the averaged peak area ratio from the 3 samples (30 patterns) at each age was further normalized by its maximum value obtained at all the hydration ages. This method was applied to the peaks for silica fume, CH and calcium silicates ($C_3S + C_2S$), in the UHPC patterns.

Figure 5 shows the evolution curve obtained for silica fume by this quantitative analysis method. It is observed that silica fume is decreasing with a high rate during the first week after mixing. It can be due to the fact that silica fume is an active pozzolanic material that reacts quickly with CH at the very early age. Then, decreasing trend is almost ceased for the next following two weeks. This indicates that the pozzolanic reaction slows down after a week or two.

Figure 5. Evolution of peak area for silica fume in UHPC (vertical dashed bars show standard deviation)

The evolution curve for CH in the UHPC matrix is shown in Figure 6. This curve shows that the CH content increased during the first week after mixing. Thereafter, the content decreased rapidly till 14 days and then it only decreased slightly. This trend corresponds well with the changes of silica fume. The increased amount at the early age is due to the hydration of calcium silicates, while the decreased CH during 7 to 14 days can be attributed to its faster consumption by silica fume than the formation from calcium silicates hydration. The lower reactivity of both calcium silicates and silica fume after 14 days led to only minor decrease in CH content during this period.

Figure 6. Evolution of peak area for CH in UHPC (vertical dashed bars show standard deviation)

The evolution of calcium silicates in the UHPC matrix can be seen in Figure 7. It is observed that the amount of calcium silicates decreases with hydration age consistently. This can be simply explained by reduction in content of calcium silicates due to hydration in presence of water and production of calcium hydroxide.

Figure 7. Evolution of peak area for calcium silicates in UHPC (vertical dashed bars show standard deviation)

3.3 Conventional cement paste

Figure 8 depicts the spectrum for the conventional cement paste at 3 days. The pattern for the UHPC matrix at the same hydration age (Figure 3) is also displayed in the figure for comparison. Similar to UHPC matrix, both the unreacted cement ingredients and hydration products can be found in the conventional paste, including calcium silicates (C_3S & C_2S), ettringite, and calcium hydroxide (CH). But these peaks were also noted to be much stronger in the conventional paste. . This is due to the much higher amounts of cement used in the conventional cement paste than in UHPC (Table 3).

Figure 8. Spectra comparison between UHPC and conventional cement paste hydrated at 3 days

To be consistent with the UHPC matrix, the conventional paste was also tested from 3 days to 28 days after mixing. Figure 9 stacks Raman spectra obtained from the conventional paste. From these patterns, calcium silicates (C_3S and C_2S), ettringite, and CH are consistently found at all the hydration ages. For calcium silicates, different from the patterns of the dry powder (Figure 1), the peak intensity for C_2S is always higher than C_3S in the

patterns during the measuring framework. This is caused by the higher reactivity of C_3S at the early age, leading to its faster consumption during its early age. It is also noticeable from the stacked patterns that the intensities of calcium silicates peaks decreased gradually with the increasing hydration ages. On the contrary, as one of the hydration products of calcium silicates, CH increased at the hydration ages from 3 to 28 days. From the figure, one can also see the decreased intensity of ettringite at late age. In all the patterns, the peak for C_3A was not detected, attributing to its reactive hydration at the very early age (before setting).

Figure 9. Stacked spectra for conventional cement paste with a w/c ratio of 0.60 at the hydration ages from 3 to 28 days

For the conventional paste, quantitative analysis was also applied to the peak areas for calcium silicates (C_3S+C_2S) and CH. The averaged quotient from the 3 samples (30 patterns) at each age was further normalized to the maximum averaged value obtained at all the hydration ages. Figure 10 exhibits the quantitative analysis results of the peak area for calcium hydroxide in the cement paste. By comparing Figures 6 and 10, it can be seen that the evolution of CH in the conventional paste increase steadily with hydration age,

while the CH peak area decreases after 7 days in UHPC matrix. This is a good indication of the capability of the RS method to identify different hydration mechanisms: conventional and pozzolanic.

Figure 10. Evolution of CH peak area in conventional cement paste (vertical dashed bars show standard deviation)

Figure 11 shows the evolution of peak area for calcium silicates in conventional paste. According to this figure, the amount of calcium silicates is decreasing at the increased hydration age, especially during the first two weeks. This is caused by the more reactive hydration of calcium silicates (mainly C_3S) at the early age. However, the decreasing trend of the peaks was almost terminated after two weeks. At this stage, the hydration of C_2S dominates the ongoing reactions of calcium silicates, and the C_2S reaction is known to be much slower than C_3S . It should be noticed that the faster consumption of calcium silicates for the first two weeks corresponds very well with the faster generated CH amount for the same hydration period as shown in Figure 10. And the development trends are constant from 14 to 28 days for both materials. This hints the reliability of the Raman analysis on the hydration progress.

Figure 11. Evolution of peak area for calcium silicates in conventional cement paste during hydration (vertical dashed bars show standard deviation)

4. Conclusion

The results of this study show that Raman spectroscopy is a method that can be used to monitor the hydration process in different cement pastes. It is capable of identifying and tracking different cement components and hydration products at different hydration ages. This enables Raman spectroscopy to distinguish different hydration mechanisms in the hydration process involved in Portland cement paste and UHPC. In particular, the following conclusions can be drawn:

- 1) RS is capable of identifying different clinker phases, including C_3S , C_2S , C_3A , and C_4AF in cement. It can also differentiate ordinary type I cement from class H oil well cement.
- 2) Although silica fume, silica flour, and silica sand all have very similar chemical components, their characteristic peaks can be easily identified and recognized by RS.
- 3) By applying quantitative analysis on RS patterns, it was found that silica fume is more reactive at early ages (first two weeks).

4) The quantitative analysis shows that RS is sensitive enough to differentiate conventional hydration progress and pozzolanic reaction. The comparison of calcium hydroxide development trends in UHPC and conventional paste is a good indication of that.

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