Technical Report

Chemical Imaging of Distribution of Hydrates Using Raman and Photoluminescence Spectroscopy

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Abstract

Raman microscopy is a chemical imaging method used to visualize the distribution of chemical structure with a spatial resolution of several hundreds of nm by combining Raman spectroscopy and an optical microscope. This paper describes not only the principle of Raman microscopy, but also its application to the chemical imaging of cement hydrates. We analyze the distribution of $Ca(OH)_2$ in cement paste to understand the influence of curing temperature and curing time on the distribution. Furthermore, we show that the Raman microscope allows us to observe not only Raman bands caused by specific vibration modes, but also photoluminescence signals, a type of fluorescence. Chemical imaging of various types of hydrates will be archived by using both Raman bands and photoluminescence signals as fingerprint peaks.

1. Introduction

Chemical reactions involving water play important roles in iron making processes. In the formation of pseudo grains for iron ore sintering and that of non-burnt pellets, for example, hydrated binders such as burnt lime and cement mainly account for the compact strength.

Among different types of cement, Portland cement (hereinafter referred to often simply as cement) is used widely for the production of non-burnt pellets.^{1,2)} Detailed analysis of its hydration reactions and the distribution of product hydrates could yield suggestions for more effective use of its binding function. As will be explained later, however, since Portland cement is a mixture containing various minerals, and different hydration reactions take place in parallel at the same time, analysis of its hydrating and hardening mechanisms cannot be performed without difficulty.

Portland cement comprises alite $(3\text{CaO} \cdot \text{SiO}_2)$, belite $(2\text{CaO} \cdot \text{SiO}_2)$, aluminate $(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$, ferrite $(4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3)$ and gypsum (CaSO_4) ,³⁾ and when mixed with water, all these component phases are dissolved by hydration. It is generally considered that hydrates form from these components to fill in the voids between grains, bringing about binding strength.⁴⁾ Various types of hydrates are involved herein: while typical examples include calcium silicate hydrate ($n\text{CaO}-m\text{SiO}_2$ -H₂O, hereinafter called C-S-H), ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), monosulfate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$.

 $12H_2O$), and calcium hydroxide (or portlandite Ca(OH)₂),⁵⁾ there are reports on other hydrates of unknown structure.⁶⁾

It is possible to examine the bulk change in the chemical structure resulting from cement hydration by methods such as solid nuclear magnetic resonance (NMR)^{7–9)} and powder X-ray diffractometry (XRD).¹⁰⁾ Since it is necessary to crush the object material being analyzed into powder as the pretreatment for these analytical techniques, the positional relationship between hydrates and unreacted minerals is lost during the crushing. Through a scanning electron microscope (SEM), on the other hand, although it is possible to obtain information on the shape of hydrates and component elements, it is quite difficult to distinguish different hydrates of similar chemical composition and attribute a certain reaction product to a specific molecular structure.

The Raman microscope, as a combination of Raman spectroscopy and an optical microscope is a promising method that overcomes the above two issues: allowing us to distinguish chemical structure without losing positional information.¹¹ By this combined method, a laser beam is irradiated onto a target point in an optical image of an object material and the Raman spectrum from the point is collected. Since the Raman spectrum contains information on the symmetry of the molecule and its vibration mode, it is possible to define the chemical structure of the molecule based on the information of Raman spectrum. In addition, by continuously recording Raman

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spectra, it is possible to understand the species of chemical structure and their distribution. Based on the visualized information, it should be possible to specify the structure that exerts a certain function. Such imaging of molecular functions based on the information of chemical structure, which is called chemical imaging, has been applied in the pharmaceutical industry to evaluate the distribution of a specific ingredient within tablets.¹²⁾ Some studies have reported the application of Raman spectroscopy in the field of cement,^{13–19)} but few have extended the application to imaging of the distribution of hydrates.

In consideration of the above situation, this paper reports a chemical imaging technique of the distribution of cement hydrates by using a Raman microscope.

2. Body

2.1 Principle of Raman spectroscopy

Raman spectroscopy is a method for analyzing weak lights scattered from an object to which a light beam is irradiated. When an incident light is assumed to be a vibrating electric field, molecules in the object are subjected to an external force of the electric field. As a result, an induced dipole moment forms inside each molecule, which causes the emission of electromagnetic waves, and these waves are detected as scattered light. **Figure 1** schematically illustrates the principle of the Raman scattering. When a monochromatic incident light beam of a specific wavelength (frequency v) excites a sample, the above light scattering takes place. The scattered light consists of three components. Most of it has the same wavelength as the incident light, and is called Rayleigh scattering.

The other two components are the Stokes scattering of a lower frequency (longer wavelength) than the incident light and the anti-Stokes scattering of a higher frequency (shorter wavelength); these two constitute Raman scattering. Because the intensity of the Stokes scattering is greater than that of the anti-Stokes scattering, most Raman spectroscopic analysis uses the former in consideration of the signal/noise ratio. On the other hand, although weaker than the former, the latter is less affected by fluorescence and radiation heat, and therefore it is more suitable for advanced analysis and experiments at high temperatures. The Stokes scattering was observed in the Raman spectroscopy of the present study.

Assuming the intensity of the exciting laser (the incident light source) to be I_0 , the frequency of the incident light v, the number of light scattering molecules N, the polarizability of molecules α , and the amplitude at normal vibration frequency Q, the intensity I of a Raman signal is expressed by the following equation:²⁰⁾

$$I \propto v^4 I_0 N \left(\frac{\partial \alpha}{\partial Q}\right)^2 \tag{1}$$

This equation indicates that in order for a sample to exhibit a Raman activity and emit scattering detectable by a Raman spectrometer, it is necessary for the polarizability α of sample molecules to change. **2.2 Raman microscope**

As schematically shown in Fig. 2, a Raman microscope comprises, as main components, a microscope, a spectrometer, a detec-



Fig. 1 Raman scattering phenomenon caused by interaction between incident light and material



Fig. 2 Schematic explanation of a typical Raman microscope

tor and an excitation laser.

An electric motor driving stage is mounted on the microscope, which is basically an optical microscope. The combination of the Raman spectroscopy and a microscope enables the detection of spectra at a desired position, and thus, it is possible to measure a spectrum from a small amount of a sample, and in addition, spectra from a wide sample area by synchronization of a spectrometer and a stage.

Due to the use of confocal optical system, which has become popular recently, signals of fluorescence, scattered light, etc. from matrixes other than a focal position are reduced, and it is now possible to efficiently observe the Raman spectra of a desired object. As for the incident light source, continuous emission type lasers are used for many systems. Different types of lasers such as gas lasers (argon ion lasers, etc.), semiconductor lasers and solid-state lasers can be selected according to the aim of the analysis in consideration of the desired wavelength ranging from ultraviolet, visible to near-infrared. For Raman spectroscopy, it is necessary for the excitation light source to stably emit a laser beam with 1 cm⁻¹ or less in width continuously for a long period. To detect all the Raman spectra from a chosen area throughly, the latest types of Raman microscopes are equipped with the laser beam scanning method, the stage scanning method or both.

The spectrometer is basically composed of a single or triple monochromator equipped with a diffracting grating. At a front-stage part of the monochromator, there is a filter that attenuates the Rayleigh scattering selectively. An edge filter or a notch filter is commonly used for the purpose; whereas only the Stokes scattering is detected with an edge filter, both the Stokes scattering and the anti-Stokes scattering can be detected with a notch filter. When the scattered light after going through a filter enters a monochromator, it is dispersed and finally reaches the detector. When the number of the rulings of the diffraction grating is small, Raman spectra of a wide range of wave numbers can be acquired, while the wave-number resolution becomes poor. In contrast, when there are many rulings, the wave-number resolution is improved, though in a narrower range of wave number, and it is also possible to reduce background noises such as stray light. However, when the number of the rulings is large, higher operational accuracy and stability are required for the hardware.

A CCD detector having elements, each about $20 \times 20 \ \mu m$ in size, arranged two-dimensionally is widely used as the detector. The CCD detector exhibits a characteristic wavelength sensitivity, that is, its sensitivity depends on the wavelength.

The following hardware was used for the present study: a Raman microscope of the model Raman11 manufactured by Nanophoton Corporation; an excitation laser that emitted visible light of 532 and 488 nm wavelengths; and diffraction gratings of 600 and 1200 gr. As explained herein later, the light intensity of the excitation laser and the exposure time were set such that the sample would not be damaged.

2.3 Sample preparation

Specimens of hardened cement were prepared in the following manner. Table 1 shows the chemical composition of the Portland

cement used; it contained Ca, Si, Al, and Fe, etc. as main constituent elements. After water addition by 40 mass% to cement, it was stirred for 60 s, cast into molds, and then cured for a prescribed time at the prescribed temperature. The hardened cement specimens were extracted from the molds, and to stop the hydration reaction, repetitively immersed in acetone to remove free water under reduced pressure. Thereafter, all the specimens underwent a compressive strength test, were embedded in resin, and then the section surfaces were polished under dry condition: using no water during the polishing.

2.4 Optimization of measurement condition

Before analysis using a laser Raman microscope, it is necessary to carefully set the intensity of the laser beam and the exposure time. Especially, the compounds such as hydrates that seems to be damaged by heat will be disintegrated and the information of its structure, which is the real target of the analysis, must be lost if the power of excitation laser beam is too strong. On the other hand, if the beam is weak, the damage can be avoided, but it will take a long time to obtain a sufficiently high spectral intensity although the damage can be avoided.

In view of the above, the best laser intensity and exposure time were defined using the hardened cement specimens after curing. **Figure 3** shows the relationship between the laser power and the exposure time to cause thermal damage to the specimens. The graph shows that, with an objective lens of 20 times magnification, which is used most commonly, it is possible to irradiate a laser beam with power of 0.4 mW for as long as 60 s.

Based on the above finding, the Raman microscopic imaging was conducted using a 20-times magnification objective lens and irradiating a laser beam of a wavelength of 532 nm at the output power of 0.1 mW for an exposure time of 30 s.

2.5 Spectroscopy imaging of calcium hydroxide Ca(OH),

Raman spectra of typical hydrates of cement are given in **Fig. 4**. Note here that the range from 1 500 to 3 000 cm⁻¹, where no characteristic bands were recorded, is omitted from the graph. The vibration modes were attributed to respective substances based on past



Fig. 3 Relationship between laser power and exposure time to cause damage to speciemen

Table 1 Chemical compositions of portland cement

	(mass%											
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO3	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	I.G. loss	
65.1	20.3	5.36	3.00	1.02	1.87	0.21	0.23	0.29	0.25	0.25	2.18	



Fig. 4 Raman spectra of cement hydrates The C/S means basicity defined by the ratio of CaO (mass%)/SiO₂ (mass%).



Fig. 5 Raman imigaes of Ca(OH), in cement pastes during hardening at different curing tempeatures

studies.^{13, 15, 17, 18, 21)} Since hydrates mostly contain OH groups and H_2O molecules, vibration modes resulting from their stretching were observed in the range over 3000 cm⁻¹. However, hardened cement actually exhibits few spectral patterns as clear as those in this graph, because the chemical structure of C-S-H with fine texture show wide variation, and consequently the spectral curves are likely to be affected by widely distributed background noises arising from stray lights. In contrast, calcium hydroxide Ca(OH)₂ demonstrates a very sharp stretching mode of OH at 3619 cm⁻¹. Since this band is stronger than the OH stretching modes of the other hydrate compounds, it can be distinguished easily.

Based on the above consideration, an imaging of Ca(OH)₂ was attempted using the OH stretching Raman band described above. Spectra were measured in an area of roughly 170 μ m squared using a Raman microscope, and the distribution of Ca(OH)₂ was visualized based on the vibration mode at 3619 cm⁻¹.

Figure 5 shows imaging of the change in the Ca(OH), distribu-

tion in the cement specimens over time during curing at different temperatures. In these frames, $Ca(OH)_2$ images in red are superposed at a transmittance of 70% on optical microscope images of the cement specimens.

It is clear from these frames that, when the specimens were cured at 25°C, the ratio of $Ca(OH)_2$ significantly increased over time. In contrast, when they were cured at 80°C, $Ca(OH)_2$ crystallized in considerable amounts as early as 6 h of curing, but after that, the change in its amount over the curing time was small.

From the above images, the area ratio of Ca(OH)₂ was calculated and plotted in **Fig. 6** in relation to compressive strength. The graph indicates that at a curing temperature of 25°C compressive strength increases with the increase of Ca(OH)₂. At curing temperatures of 50 and 80°C, in contrast, no distinct relationship is seen between the strength and the area ratio of Ca(OH)₂; when the curing temperature was 80°C, for instance, although compressive strength increased with curing time, the area ratio of Ca(OH), remained sub-



Fig. 6 Relationship between area ratio of Ca(OH)₂ and compressive strength

stantially unchanged.

This is probably because, at a curing temperature of 25°C, compressive strength increased mainly as a result of a void-filling process such as the formation of C-S-H and Ca(OH)₂, while compressive strength at the curing temperature of 50 or 80°C increased mainly by the formation of covalent bonds through the dehydration reaction of C-S-H.

2.6 Possibility of C-S-H imaging using photoluminescence

As shown in Fig. 4, since the vibration modes originating from H_2O molecules and OH groups in C-S-H are broad and their intensity is low, it is quite difficult to distinguish spectral bands assigned to C-S-H when it coexists with other hydrates. If it becomes possible by some technical improvement to visually show C-S-H distribution based on its clear spectral bands, it will be a significantly useful solution.

Therefore, I reviewed the Raman band of C-S-H and studied the possibility of its imaging. Figure 7 shows the Raman spectra of C-S-H in a high-frequency range; when the range of analysis was expanded up to 4500 cm⁻¹ with an excitation beam of 532 nm wavelength, two spectral bands were detected at a wave number of 4400 cm⁻¹ approximately;²²⁾ the bands had not been observed in the Raman spectrum of Ca(OH)₂. Since the wave number of Raman scattering is generally considered to range roughly from 100 to 4000 cm⁻¹, the two detected bands cannot be viewed as being simple vibration modes; they may have possibly been caused by (1) combination or harmonic tones, (2) resonance or (3) other physicochemical phenomena. To eliminate the possibility of its being caused by factors of the equipment, the same samples were analyzed using a Raman microscope, model NSR7000 (JASCO Corporation). As a result, the same spectral bands were observed at the same wave numbers, which verified that they were of the specimen origin.

The analysis was repeated using excitation laser beams of different wavelengths, 488 and 785 nm. As a result, the bands in question disappeared, which eliminated the possibility of their being caused by the combination or harmonic tones. Their resulting from resonance is theoretically unlike either, and could not be rationally explained in consideration of various conditions.

Based on the result that the spectral bands in question depended on the wavelength of the excitation beam, it is suggested that they



Fig. 7 Raman spectra in high wavenumber region of synthesized C-S-H samples

were a type of fluorescence, more specifically, photoluminescence (PL). Assuming the wavelength of the incident laser beam to be λ_1 (nm) and that of the scattered light λ_2 (nm), the wave number Γ (cm⁻¹) of normal Raman spectra is expressed by the following equation:

$$\Gamma = \frac{1}{\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)} \times 10^7 \tag{2}$$

According to this equation, the wavelength of detected Raman scattering changes depending on the wavelength of the excitation beam, while the wave number does not. It follows, therefore, that a Raman spectrum of a specific vibration mode can be detected in the same wave number even if the wavelength of the excitation beam is different.

On the other hand, the wavelength of PL detected at observation does not change depending on that of the excitation laser beam. According to equation (2), therefore, if what was detected was PL, its wave number changes inevitably depending on the wavelength of the excitation beam. From equation (2), the two spectral bands detected at wave numbers of 4366 and 4397 cm⁻¹ with an excitation beam of a wavelength of 532 nm correspond to wavelengths of 692.9 and 709.2 nm, respectively. If we forecast the wave numbers of the two spectral bands when the wavelength of the excitation beam is changed to 488 nm, we obtain through equation (2) wave numbers of 6060 and 6091 cm⁻¹, respectively.

Based on the above, after setting of the center of the observation wave number range at 6050 cm⁻¹, the bands were searched under conditions suitable for the forecasted wave numbers and with an excitation wavelength of 488 nm, and as a result, signals were detected at 6060 and 6091 cm⁻¹ as shown in **Fig. 8**. This verified that the two spectral bands detected roughly at the wave number of 4400 cm⁻¹ with an excitation beam of 532 nm wavelength resulted from PL. The wavelengths of the PL ranged from 690 to 710 nm, longer than those of the excitation laser beams, 532 and 488 nm, which means that the energy has been lost during the luminescence process. This is presumably due to a part of the energy being lost as heat during the transition from the excitation state to the ground one.

Although the luminescence efficiency of the PL was measured by quantum yield method, it failed to observe any clear peaks of PL in the wavelength range of 690 to 720 nm, presumably because the intensity of the PL was actually so weak that it could be detected by reducing the other fluorescence signals owing to the use of the confocal Raman microscope.

Figure 9 shows examples of cross sectional imaging of granules prepared by mixing synthetic C-S-H and Fe₂O₃ particles based on

the PL signal at 4397 cm⁻¹ in wave number. While C-S-H was distributed homogeneously in area shown by fine particle with white color, it also aggregated locally as marked with circles. As stated above, a Raman microscope allows us to observe PL as well as Raman spectral bands. It will, therefore, become possible to perform chemical imaging of various substances, which has hitherto been impossible, if we examine Raman spectra from a new point of view and effectively use signals contained therein.

3. Conclusions

Chemical imaging of the distribution of cement hydrates using the Raman and PL spectroscopy was studied, and the following findings were obtained:

- 1) The OH stretching mode of calcium hydroxide Ca(OH)₂ exhibits a clear Raman band at a wave number of 3619 cm⁻¹. It is possible by using this band to visualize the distribution of Ca(OH)₂ without the interference of other hydrates.
- 2) By visualizing the distribution of Ca(OH)₂ in hardened cement, and quantifying its amount in terms of area ratio at a cross sec-



Fig. 8 Raman spectrum of C-S-H(C/S=1.4) obtained at 488 nm excitation laser

tion, it is possible to analyze the influence of curing temperature and time over the growth of Ca(OH),.

3) C-S-H hydrates emit PL lights having wavelengths (690 to 710 nm) longer than those of visible excitation lights (532 and 488 nm). The PL lights were used for producing chemical images of hydrates at cross sections of test granule specimens, and the hydrates were found to aggregate locally.

Combined use of the Raman and PL spectroscopy is expected to greatly advance chemical imaging of hydrates in hardened cement.

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Fig. 9 Photoluminescence imaging of granules of iron oxide (Fe₂O₃) mixed with synthesized C-S-H

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