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Anomalous fluorescence in near-infrared Raman spectroscopy of cementitious materials

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Abstract

The results of near-infrared Fourier transform Raman spectral examination of cement minerals, several commercial Portland cements, and hydrating Portland cements are critically examined. It is shown that structured fluorescent effects dominate the observed spectra for C_3S, C_2S, and cement, and none of the bands generated by this mode of examination is a true Raman band. The apparent bands for the Portland cements are in different positions to those for the individual cement minerals. The fluorescence-derived spectra for different cements are similar to each other but vary enormously in intensity for different cements. Hydration progressively reduces the intensity of the bands, but does not generate bands at new locations. It is tentatively suggested that the fluorescence effect may be somehow associated with the status of the cement components as orthosilicates (i.e., composed of isolated silica tetrahedra. Samples of high-purity C_2S exhibit the fluorescence effect, but samples of CS (wollastonite) of similar purity do not. The latter are metasilicates (i.e., composed of linked chains of silica tetrahedra). They exhibit normal Raman Stokes and anti-Stokes bands.

Keywords: Spectroscopy; Raman spectroscopy; Fluorescence; Ca_3SiO_5; Ca_2SiO_4

1. Introduction

The potential of Raman spectroscopy as an analytical technique for cementitious materials was first demonstrated by Bensted [1–3], nearly three decades ago. Subsequently, Conjeaud and Boyer [4] successfully used a Raman microprobe to study individual crystals in clinker phases and Portland cements. Since this time, however, Raman spectroscopy has been used only sparingly to study such materials, probably in part because of strong fluorescence effects generated for many substances under both visible and near-infrared excitation modes.

It was generally considered that the development of Fourier transform (FT) Raman spectroscopy with near-infrared excitation in 1986 should eliminate the usual problems of fluorescence experienced in many dispersive Raman examinations by precluding electronic absorption of the incident radiation [5]. Unfortunately, FT Raman studies of cementitious materials with near-infrared excitation have generated ambiguous results. Dyer et al. [6] observed a "very unusual result concerning the intensity of the spectra" for near-infrared FT Raman spectra of cement minerals, and concluded that the origin of the bands was probably fluorescence rather than Raman scattering, but these authors were unable to identify the fluorescing species. Subsequently, Bonen et al. [7] published near-infrared FT Raman

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spectra of cement minerals, and allocated the bands observed to Raman scattering from various silicate vibrations rather than to fluorescence. A similar ambiguity exists in the literature for near-infrared FT Raman spectra of calcium phosphate minerals such as apatite [8–12].

One way of confirming that a given band exhibited in the usually determined (Stokes) Raman spectrum is truly a Raman band is to investigate the existence, or lack of it, of a corresponding band in the anti-Stokes Raman spectrum. The demonstration that an anti-Stokes Raman band exists corresponding to a given Stokes Raman band would confirm its identification as a true Raman band [13]. Another confirmation technique is to demonstrate that the band in question occurs at the same Raman shift wavenumber independent of the particular excitation wavelength used [13]. Neither of these checks has been previously applied to cement minerals or cements. Since most anti-Stokes bands are inherently of weak intensity, the second alternative is more generally applicable.

In the present work, we report Raman spectra obtained for both near-infrared and visible light excitation on cement components and on several different Portland cements. Progressively hydrating cement pastes were also examined, but only using near-infrared excitation. Our aim is to clarify the interpretation of FT Raman spectra of these materials, and to assess the general applicability of the technique to the study of cement systems.

2. Experimental

The major components of cements are the tricalcium and dicalcium silicates, alite, and belite, which have the nominal compositions Ca_3SiO_5 and Ca_2SiO_4 and are given the symbols C_3S and C_2S in cement nomenclature. Also present in cements are tricalcium aluminate (nominal composition $Ca_3Al_2O_6$, denoted C_3A), tetracalcium aluminate ferrite (nominal composition $Ca_4Al_2Fe_2O_{10}$, denoted C_4AF), and calcium sulfate, as well as numerous other minor phases. Synthetic preparations of pure C_3S, C_2S, C_3A, and C_4AF (Construction Technology Laboratories, Skokie, IL, USA) were investigated in this work. The high iron content of C_4AF precluded acquisition of its Raman spectrum. Three Portland cements obtained from three different US suppliers, labeled A, B, and C, were also examined. Their oxide compositions, determined by X-ray fluorescence analysis, are reported in Table 1. Some supplementary determinations were also carried out with several high-purity calcium silicates obtained from commercial sources.

Table 1
Oxide composition of cements (all values reported in mass percent)

Oxide	Cement		
	A	B	C
SiO_2	21.8	20.35	20.09
Al_2O_3	4.21	4.44	4.58
Fe_2O_3	3.23	3.48	2.37
CaO	65.1	62.86	65.15
MgO	1.04	3.07	2.33
SO_3	2.58	2.64	2.41
Na_2O	0.22	0.10	0.22
K_2O	0.67	0.66	0.41
TiO_2	0.18	0.32	0.24
P_2O_5	<0.018	0.03	<0.015
Mn_2O_3	0.03	0.53	0.06
SrO	0.00	0.00	0.08
LOI	0.81	1.46	1.93

Near-infrared Raman spectra (both Stokes and anti-Stokes) were collected using a Nicolet 910 FT Raman spectrometer equipped with a Nd:YAG laser (1064 nm) and liquid nitrogen-cooled germanium detector. The useful spectral range covers approximately from 200 to 3600 cm^{-1} for Stokes radiation and from 200 to 970 cm^{-1} for anti-Stokes radiation. Less than 50% of the maximum laser power (1 W) was used for each measurement. A 180° reflective optical geometry was used for data collection. The resolution was 2 cm^{-1}, averaging 100 scans per sample (for a total integration time of 150 s per spectrum). Spectra were corrected for instrument response, which was determined using a white light source and a nonabsorbing and non-Raman scattering specimen of KBr.

Visible Raman spectra (Stokes radiation only) were recorded under a dispersive Renishaw System 1000 Raman microscope using 514.5-nm Ar^+ and 632.8-nm HeNe lasers with 4 mW power measured at the sample and a total integration time of approximately 300 s per spectrum. A spot size of approximately 40 μm was used to achieve adequate sampling of the bulk. In addition to the spectra obtained for cement components and commercial Portland cements, near-infrared spectra were determined for progressively hydrating cement pastes. These pastes were prepared by mixing 12.5 g of each of the cements with 5.0 g of distilled water for 60 s using a hand mixer. Pastes were cast and stored at room temperature in 10-ml glass screw-cap vials, which were also used as sample holders for the in situ near-infrared Raman spectroscopy measurements.

Finally, the near-infrared FT instrument described above was used to collect both Stokes and anti-Stokes spectra for several commercial calcium silicate products thought to be of higher purity than typical cement minerals. These materials were obtained from Alfa Aesar or Aldrich Chemical.

3. Results

3.1. Raman spectra observed for cements and individual cement minerals

Near infrared FT spectra derived from the cement minerals C_3S, C_2S, and C_3A, plotted as a function of Raman shift on both Stokes (>0 cm^{-1}) and anti-Stokes (<0 cm^{-1}) sides of the laser frequency, are shown in Fig. 1.

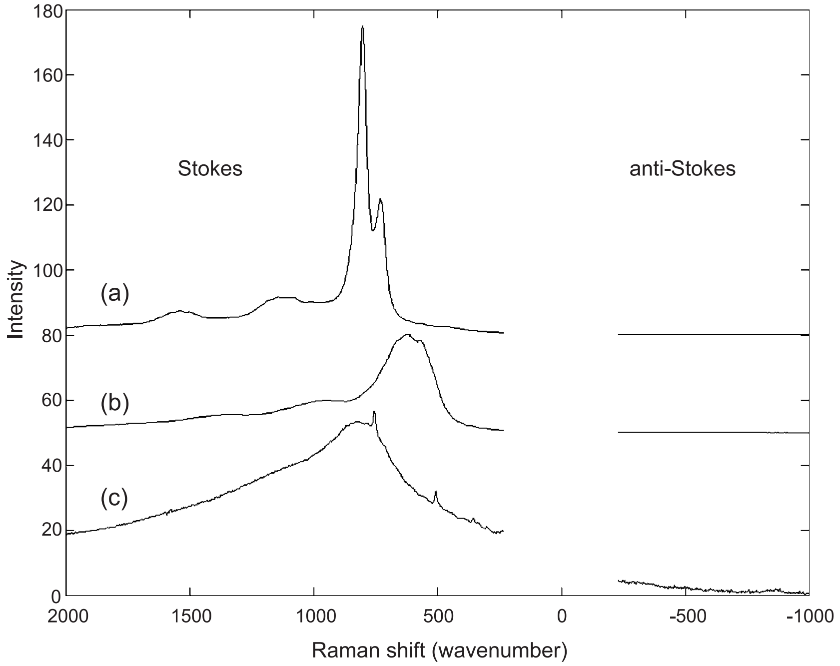

Fig. 1. Stokes and anti-Stokes near-infrared spectra of cement minerals: (a) C_2S, (b) C_3S, and (c) C_3A, plotted as a function of Raman shift (relative to the laser). Spectra (a) and (b) have been shifted vertically for clarity of presentation.

The Stokes spectrum of C_2S (Fig. 1a) exhibits strong bands at 805 and 730 cm^{-1} and weaker broad bands in the regions from 1100 to 1200 cm^{-1} and from 1500 to 1600 cm^{-1}. There are no hints in the anti-Stokes spectrum of corresponding anti-Stokes bands, even for the strongest Stokes band at 805 cm^{-1}. If this band were truly due to a Raman transition, the corresponding anti-Stokes band would have a relative intensity of approximately 3% and would have been detected.

The near-infrared Stokes spectrum observed for C_3S is significantly different from that of C_2S, and consists only of a relatively strong broad band at approximately 570 cm^{-1} and a very weak broad band at approximately 940 cm^{-1}. Again, no corresponding anti-Stokes bands appear.

Within a limited shift, there is a good agreement between the location of the C_3S peaks reported by Bonen et al. [7] using infrared FT Raman and our observations. The main difference is that the peaks in Ref. [7] are sharper, which could be a result of a smaller spot size used.

The absence of bands from all of the anti-Stokes spectra strongly suggests that bands in the Stokes region of the spectra recorded for both C_2S and C_3S in Fig. 1 originate from fluorescence rather than from Raman scattering.

For C_3A, the Stokes spectrum consists of a broad background with a bulge centered at approximately 830 cm^{-1}, with two very weak but sharp bands at 760 and 510 cm^{-1} superimposed. Although the intense diffuse background is certainly fluorescence-derived, the very small but sharp bands are identical to those detected by Conjeaud and Boyer [4] using visible light-excited Raman spectroscopy, and thus are almost certainly true Raman bands because they occur at the same Raman shift independent of the incident radiation frequency. They have been assigned to Raman scattering from Al–O stretching and bending vibrations, respectively [4].

Thus, of the individual cement components examined in near-infrared FT Raman spectroscopy, the entire C_2S and C_3S spectra are apparently due to fluorescence effects with no true Raman bands being found; C_3A exhibited strong fluorescence effects with two weak Raman bands superimposed on them.

Near-infrared FT Raman spectra observed for three commercial Portland cements designated A, B, and C are presented in Fig. 2. They are broadly similar to each other—the most striking difference among them being the very large variation in overall intensities. Note that each spectrum was recorded under the same conditions of laser power and focus; thus, the intensity variation is a function of the sample and not of technique. Moreover, five repeat measurements were made for each cement, with virtually identical results.

The spectra are not combinations of the bands previously found for the individual cement components. Neither the strong band previously observed for C_3S at 570 cm^{-1} nor the strong bands previously observed for C_2S at 805 and 730 cm^{-1} are present in the corresponding cement spectra. Rather the most prominent band in each cement spectrum is observed at about 650 cm^{-1}, with broad bands centered at approximately 1000 and 1400 cm^{-1} also being found. The observed spectra for cements A and B contain a shoulder at 800 cm^{-1}, and the latter contains an additional band at approximately 1130 cm^{-1}. Again no anti-Stokes bands were observed, with the cements being similar in this regard to the individual cement minerals.

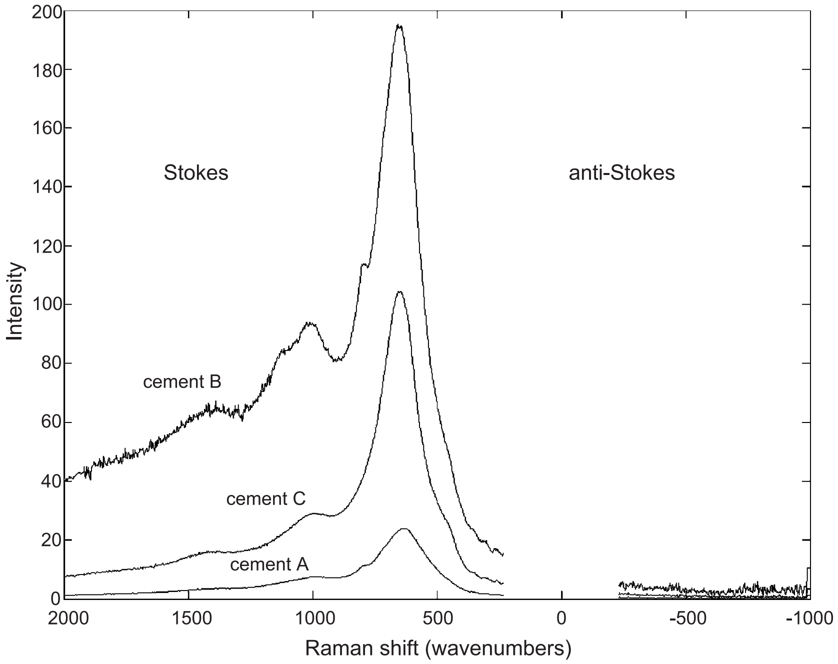

Fig. 2. Near-infrared FT spectra of cements A, B, and C (Table 1).

The above results suggest that all of the bands exhibited by the cements are due to fluorescence effects, with the effects being common to all of the cements, but exhibited at locations different from those found for the individual cement minerals previously studied.

Fluorescence phenomena are dependent on the wavelength of excitation, and peaks due to fluorescence may shift or completely appear or disappear dependent on the excitation source, and nature and level of impurities in the material, thereby limiting its potential use. Impurities, even in trace amounts, can give rise to spurious fluorescence bands. Raman scattering, however, is independent of the wavelength, and the Raman spectrum so obtained is a fundamental characteristic of the material under study.

As indicated earlier, one test for deciding whether a given spectral band is due to the Raman effect or to fluorescence is to monitor its Raman shift under different excitation wavelengths. Genuine Raman bands will occur at the same frequency relative to the excitation frequency (i.e., will exhibit the same Raman shift under different excitation wavelengths); in contrast, bands due to fluorescence will either remain at the same absolute frequency (rather than at the same Raman shift relative to the laser), or may disappear altogether.

The former effect is demonstrated in Fig. 3 for the C_3S sample. Two different visible light Raman spectra were recorded successively using excitation at two different visible light wavelengths, 514.5 and 632.8 nm. The two visible light spectra have strong bands at identical positions, confirming that they are true Raman bands. The spectra bear no resemblance to the near-infrared FT Raman spectrum of the same sample shown in Fig. 1, thus confirming the non-Raman origin of the bands in Fig. 1. Similar results were observed for C_2S and the cement samples. It should be noted that true Raman C_3S bands exhibited in Fig. 3 are very similar to those reported by Conjeaud and Boyer [4] for visible light excitation. The bands at 840 and 890 cm^{-1} found in both visible light spectra of C_3S can be assigned unambiguously to silicate stretching vibrations [14]. The broad and weak band at approximately 550 cm^{-1} is probably due to silicate bending vibrations. The sharp band at 1087 cm^{-1} is assigned to the totally symmetric v_1 stretching vibration of carbonate [14], presumably indicating degradation of the sample from atmospheric CO_2 attack. The doublet at 1368 and 1398 cm^{-1} in the HeNe spectrum not found in the Ar^+ spectrum is presumably due to fluorescence, perhaps from Cr^{3+} impurities in the C_3S [15]. However, these features could conceivably also result from plasma lines emitted by the laser or other stray (room light) sources. A diffuse fluorescence background also occurs in both spectra, somewhat more severely with Ar^+ laser excitation than with the HeNe excitation.

3.2. Origins of the fluorescent spectra found for cements

It is of interest to note that the fluorescence effects found for cements and calcium silicates using near-infrared FT Raman examination are strong and structured, giving rise to clearly defined bands. These fluorescence bands are much sharper than the diffuse background fluorescence previously acknowledged to be a problem for visible Raman spectra, and thus can be mistaken for Raman bands. These findings are in agreement with those of Dyer et al. [6] and definitely imply that the interpretations of similar spectra in terms of silicate vibrations by Bonen et al. [7] are incorrect. The origin of these fluorescence effects within cements and cement minerals is unclear.

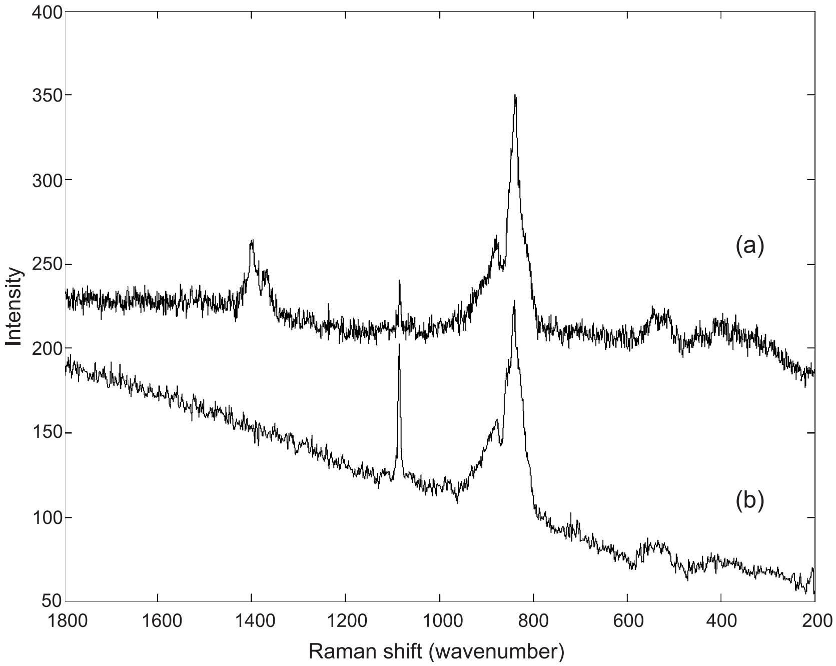

Fig. 3. Visible light Raman spectra of C_3S recorded with (a) 632.8-nm HeNe and (b) 514.5-nm Ar^+ laser excitation.

A number of reports in the literature suggest that such strong and structured fluorescence effects can be a major problem in near-infrared Raman spectroscopy of other materials, including calcium phosphates [9–11], alumina [16], and lanthanide salts [17]. In these accounts, the origin of the fluorescence is discussed in terms of the presence of trace quantities of various transition metals or lanthanides, or sometimes ascribed to lattice defects.

To investigate the possibility that trace metals are the source of the varying fluorescent effects observed for cements and cement minerals in the present work, inductively coupled mass spectrometry (ICP-MS) analysis for low-level concentrations of lanthanide metals was carried out. The results showed very low levels of lanthanides in all of the cement and cement mineral samples analyzed, with the highest concentration being approximately 30 ppm for cerium. Similar concentrations were found in each of the cements; thus, they are not correlated with the observed strong differences of the intensity of the fluorescence bands for the different cements.

In a further attempt to elucidate the origins of the fluorescence effects, attempts were made to obtain and study relatively pure calcium silicates. A dicalcium silicate sample reported to be of more than 99% purity was obtained from Alfa Aesar, and examined using the near-infrared FT instrumentation previously described. The result, as shown in Fig. 4a, exhibited two strong broad bands centered, respectively, at approximately 800 cm^{-1} and approximately 1000 cm^{-1}, with a shoulder on the latter at about 1150 cm^{-1}. These bands are not in the same locations as found for the previous specimen of C_2S as depicted in Fig. 1, and are clearly due to fluorescence (note that impurities present even at the level of a small fraction of a percent could produce fluorescence bands that are large in comparison to Raman bands).

A rather different picture emerged in the spectra of monocalcium silicates, $CaSiO_3$ (CS; mineralogically, wollastonite). Three such samples were examined. Two of these were of the same designated purity as the C_2S (more than 99% pure), the other being of lesser purity and designated as “reagent-grade.” One of the two higher-purity samples and the reagent-grade sample were obtained from the same source as the pure C_2S above; the other high-purity sample was obtained from Aldrich Chemical. CS is structurally different from both C_2S and C_3S in that the silica consists of linked chains of tetrahedra rather than of isolated silica tetrahedra as found in the cement minerals. CS does not react with water and has no cementing properties.

The spectra for the three CS samples shown in Fig. 4 are clearly different from that of the C_2S and are basically similar to each other. The spectrum in Fig. 4b was obtained from one of the two samples of stated 99% purity obtained from Alfa Aesar. It shows no apparent fluorescence effects at all, with the strong, sharp Stokes bands at approximately 980, 580, and 380 cm^{-1} being reflected in the anti-Stokes spectrum. The second CS sample of similar designated purity, obtained from Aldrich (Fig. 4c), provided an almost identical spectrum except for the broad fluorescent effect around the 980-cm^{-1} band. The reagent-grade sample does indeed show more severe fluorescent effects (Fig. 4d). Rather than structured effects giving rise to distinct bands as found in the cements and cement minerals, however, the fluorescent effect here is evidenced as a single very broad background of intensity decreasing with frequency in both Stokes and anti-Stokes regions. The effect is superimposed on the sharp true Raman spectral bands, which can just be seen.

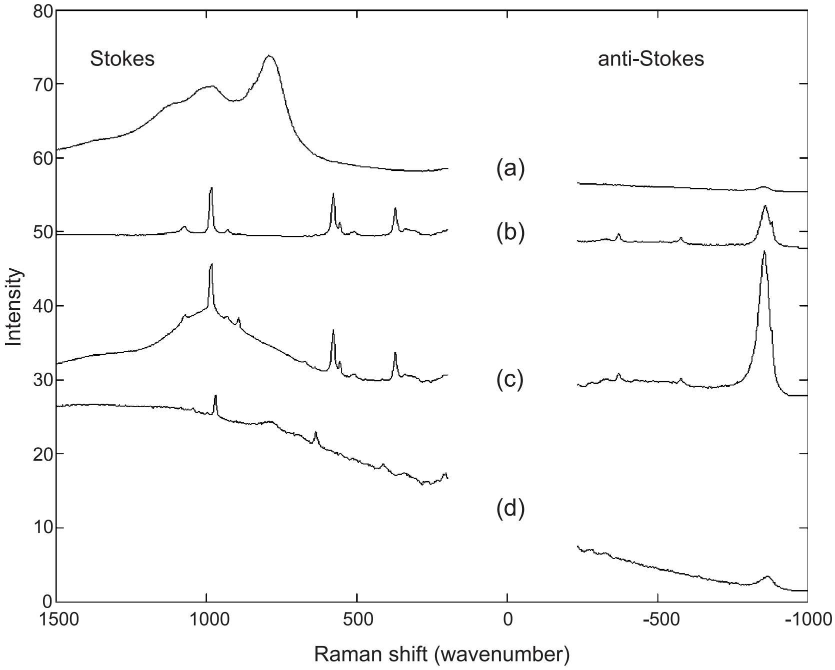

Fig. 4. Stokes and anti-Stokes spectra of various calcium silicate samples: (a) Alfa Aesar C_2S (>99% purity); (b) Alfa Aesar CS (>99% purity); (c) Aldrich CS (>99% purity); and (d) Alfa Aesar CS (<99% purity). Spectrum (a) has been scaled by a factor of 0.1 and spectra (a)–(c) have been shifted vertically for clarity of presentation.

We tentatively infer that the structured fluorescence giving rise to distinct fluorescent bands and covering up the true Raman bands for both the C_3S and C_2S cement minerals, the Portland cements, and the pure C_2S shown in Fig. 4 may be associated with the fact that all of these components are orthosilicates (i.e., are structurally composed of isolated silica tetrahedra). In contrast, for the metasilicate (linked silica tetrahedra) CS samples of Fig. 4, fluorescent effects are either absent, confined to a narrow spectral region, or spread uniformly across the spectrum. We cannot rule out the possibility, however, that an unidentified impurity present in C_3S and C_2S samples but not in the CS sample is at least in part responsible for the observed fluorescence of the former materials.

The spectra of all the calcium silicates in Fig. 4 contain an anti-Stokes shifted band at approximately 860 cm^{-1}. The relative intensity of this band is particularly high for the 99% pure CS samples (Fig. 4b and c). As it does not

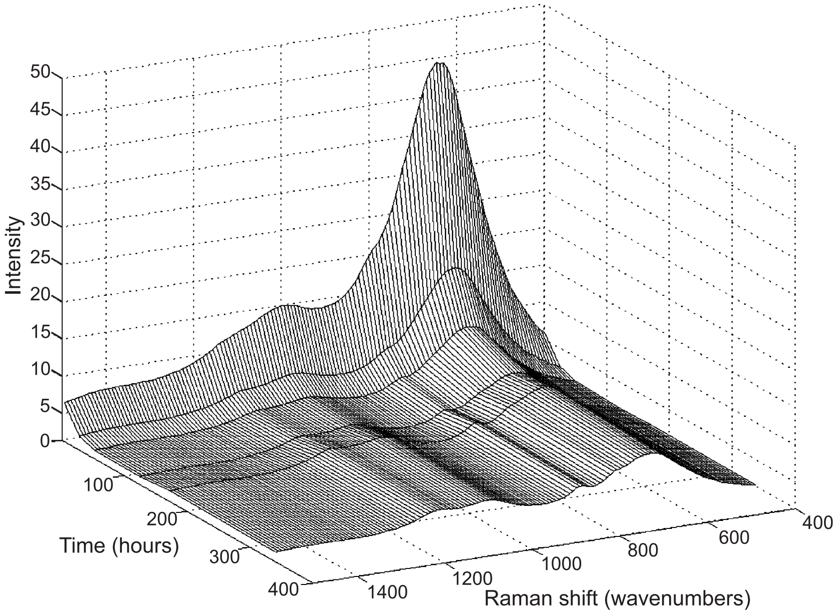

Fig. 5. In situ near-infrared FT time series spectra of cement paste A (Table 1) plotted as a function of Raman shift (relative to the laser).

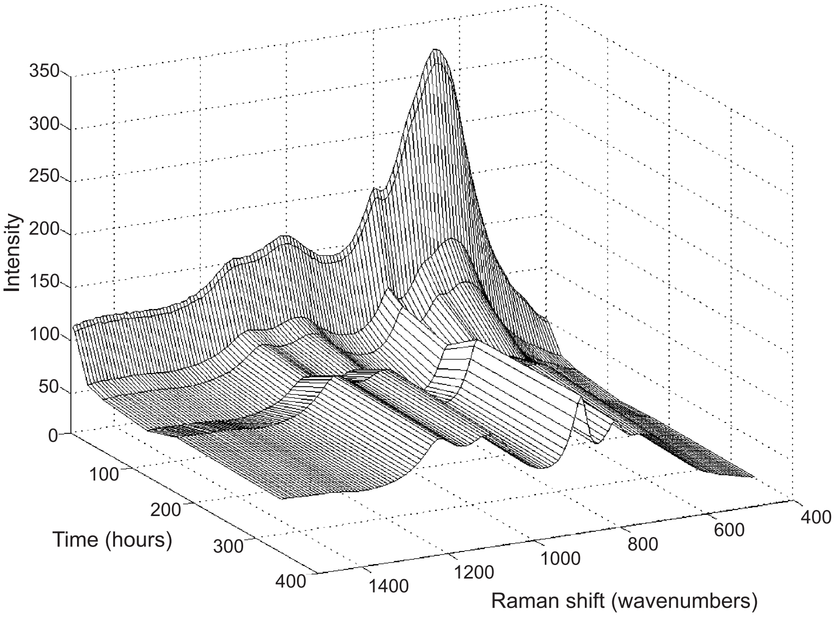

Fig. 6. In situ near-infrared FT time series spectra of cement paste B (Table 1) plotted as a function of Raman shift (relative to the laser).

correspond to a band in the Stokes side of the spectra, it is not a Raman band, although a satisfactory explanation for its origin cannot be given at the present time. It is possibly due to anti-Stokes fluorescence or to fluorescence (or plasma line emission) resulting from the HeNe laser, which is always on at very low power during data collection. Anti-Stokes fluorescence can arise, for example, from electronic excitation of vibrationally hot molecules that subsequently relax radiatively to a lower vibrational state, emitting a photon of higher energy. Alternatively, thermal excitation could occur following electronic excitation, again leading to emitted photons with higher energy than the incident photons [18]. Another possible explanation is that the anomalous anti-Stokes band results from two-photon absorption of the exciting radiation [10], although this is not considered likely given the low peak power of the (continuous-wave rather than pulsed) lasers used in this studies. Note that a similar anti-Stokes band at 821 cm^{-1} has been observed in near-infrared Raman spectra of mineral apatites [10].

3.3. Near-Infrared FT Raman spectra for hydrating cements

Figs. 5–7 show in situ near-infrared Raman spectra of pastes of cements A, B, and C recorded at irregular intervals. The period covered extends from immediately

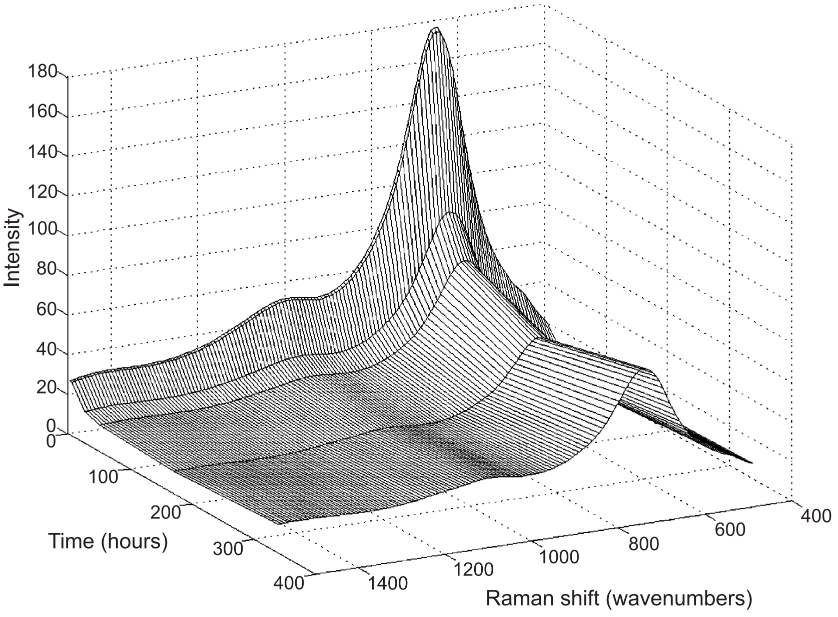

Fig. 7. In situ near-infrared FT time series spectra of cement paste C (Table 1) plotted as a function of Raman shift (relative to the laser).

after mixing to 2 weeks. As far as possible, the same instrument conditions (e.g., laser power, focus, and amplifier gain) were employed for each measurement, and in addition, a sample of C_3S powder stored in an airtight Raman tube was used as an external standard to account for instrumental drift. Each measurement was performed in triplicate, with the sample container rotated in the laser beam to account for the influence of varying sample position. The final spectrum was then taken as the average spectrum scaled according to the external standard. We found that these rather complicated procedures yielded spectra with acceptable reproducibility.

As should be expected, the zero-time spectra exhibited in Figs. 5–7 are very similar to the spectra of the corresponding unhydrated cements as previously shown in Fig. 2. Note that different intensity scales were used for the different cements in Figs. 5–7, as necessitated by the differences in spectral intensity exhibited by the parent cements.

A significant decrease in the total spectral intensity is seen after 24 h for each cement paste, the decreases being both for the background fluorescence level and in the intensity of the fluorescence-derived bands. For cement paste A, the total intensity continues to decrease at a slower rate up to 2 weeks, and there is no significant change in the relative intensities of the different bands. Similarly for cement paste C, the relative intensity of bands does not alter significantly, although the decrease in intensity levels off after 1 week. Cement paste B exhibits somewhat different behavior. Here the relative intensity of the 650-cm^{-1} band decreases more than proportionately during hydration, such that after approximately 1 week, its shoulder at approximately 800 cm^{-1} in the early-time spectra becomes the most prominent band.

Note that the most significant changes in the spectra occur between 3 and 48 h, which is the approximate time period during which much of the hydration is accomplished, especially for C_3S. The formation of dimers and eventually the polymerization of the discrete $[SiO_4]^{4-}$ tetrahedra in this phase may therefore be related to the reduction of fluorescence effects observed for the cement pastes. Also note that a comparable intensity diminution was not observed for the dry cement powders examined under similar conditions, or exposed to the laser for extended time periods (up to 4 h), thus indicating that significant photobleaching was not the cause of the reduced fluorescence of the hydrated samples. Regardless of the origin of the fluorescence effects, therefore, this progressive reduction with hydration may permit the development of a new method to monitor cement paste hydration.

4. Conclusions

It had been widely reported that the use of near-infrared excitation (Nd:YAG laser operating at 1064 nm) for Raman spectroscopy is of great benefit for reducing undesirable fluorescence—a recurring problem when dispersive visible light excitation sources are used. However, for C_3S and C_2S, and also for cements, we have found that the reverse effect occurs. The spectral bands observed with such instrumentation are due entirely to structured fluorescence effects, and the true Raman bands are covered up. These fluorescent effects result in the production of entirely different bands for the cement components when examined individually than are found for the same components in commercial Portland cements.

The overall intensities of the fluorescence effects, including both the diffuse fluorescence background and the structured bands produced by fluorescence, are very different for different Portland cements. Moreover, the intensity of the fluorescence effects found in a given Portland cement is progressively reduced as the cement hydrates.

It is tentatively suggested that the structured fluorescence effects found for C_2S, C_3S, and Portland cements may be in some fashion associated with the status of these compounds as orthosilicates (i.e., containing discrete silica tetrahedra). The structured fluorescence effects are progressively reduced on hydration (which produces dimers and eventually polymers of linked silica tetrahedra), and do not appear to be displayed with CS, which contains chains of linked silica tetrahedra rather than isolated tetrahedra.

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