Chapter 10

RAMAN SPECTROSCOPY: APPLICATION TO CEMENTITIOUS SYSTEMS

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ABSTRACT

Raman scattering was discovered by Krisma and Raman in 1928. Until approximately 1986, the Raman literature was dominated by physical and structural investigations, with relatively few reports of Raman spectroscopy applied to chemical analysis due to several technical and fundamental problems, such as weak intensity, fluorescence interference, and inefficient light collection and detection. When the introduction of Fourier transform (FT)-Raman, charge-coupled devices, small computers and near-infrared laser, the major impediments were solved and resulted in a Raman renaissance in the chemical analysis context.

Spectroscopic techniques have proved to be appropriate tools for studying cement hydration; however, fluorescence effect in anhydrous cement can give anomalous results. With the micro-Raman technique, spectra can be obtained for surface samples just a few microns thick and with minimal interference from the surrounding water. On such a scale, the interference from fluorescence, so often a problem when working with bulk cement slurry is also minimized. Spectra can be obtained rapidly and extensive sample preparation is not needed.

Recently, there has been an increasing interest in applying Raman spectroscopy to cementitious systems and to explore the potential of this technique for these materials, although it is generally less sensitive than infrared spectroscopy (IR). However, Raman spectroscopy may benefit from the possibility of a range of instrumental configurations including a variety of different laser systems for excitation and filter units for spectral purification. Moreover, the Raman microprobe instrument allows investigations on the μm-level from specific regions of a sample and it seems that this type of device/equipment is less sensitive to artifacts resulting from absorption and fluorescence.

The main objective of this chapter will be to present actual possibilities of Raman spectroscopy in the study of the cementitious systems from anhydrous to hydrate.
INTRODUCTION

Raman spectroscopy is based on the Raman effect discovery by C.V. Raman in 1928 where the measurement of the wavelength and intensity of inelastically scattered light from molecules or crystal lattices have been done.

When monochromatic light, with $h\nu_0$ energy, is scattered from a matter, this can be scattered with the same energy, $(h\nu_0)$ (Rayleigh effect) or with different energy $(h\nu_0 \pm h\nu_1)$ (Raman scattering) (Figure 1). There are two types of Raman scattering, Stokes scattering and anti-Stokes scattering. In the first case molecule absorbs energy (on the red side of the incident spectrum) and in the second situation the molecule loses energy, the incident photons are shifted to the blue side of the spectrum.

In the Raman effect, the energy differences are equal to the differences of the vibrational and rotational energy-levels of the molecule. In crystals only specific photons are allowed by the periodic structure, so Raman scattering can only appear at certain frequencies. In amorphous materials like glasses, more photons are allowed and thereby the discrete spectral lines become broad. The intensity of the Raman band only depends on the number of molecules occupying the different vibrational states, when the process began.

![Figure 1. Light scattering: Rayleigh effect, Stokes scattering and Anti-Stokes scattering](image)

These differences in energy are measured by subtracting the energy of the mono-energetic laser light from the energy of the scattered photons. The absolute value, however, doesn't depend on the process (Stokes or anti-Stokes scattering), because only the energy of the different vibrational levels is of importance. Therefore, the Raman spectrum is symmetric relative to the Rayleigh band. In addition, the intensities of the Raman bands are only dependent on the number of molecules occupying the different vibrational states, when the process began. Then lower energy states will have more molecules in them than will higher (excited) energy states. Therefore, the Stokes spectrum will be more intense than the anti-Stokes spectrum.

Typical applications of Raman spectroscopy are in structure determination, multi-component qualitative analysis, and quantitative analysis. The frequency of light scattered
from a molecule may be changed based on the structural characteristics of the molecular bonds. A monochromatic light source (laser) is required for illumination, and a spectrogram of the scattered light then shows the deviations caused by state changes in the molecule.

The first major impediment to using Raman spectroscopy is the weakness of the effect. A second problem with Raman spectroscopy is fluorescence. Fluorescence is not a scattering process, and the intensity of this fluorescence is often stronger than the scattered Raman signal, and makes any useful spectroscopic information impossible. When using an Nd:YAG laser to excite the Raman effect, the number of samples which fluoresced could be reduced. This is due to the fact that there is a reduced amount of electronic transition at the Nd:YAG laser wavelength of 1064nm. The advantage is that these low photon energies, sample heating and subsequent photochemical degradation becomes less likely.

In complex ionic crystals two distinct kinds of vibrational modes exist, external and internal ones. For the first ones well-defined complex ionic groups vibrate as rigid units and the internal modes involve atomic vibrations of the complex ionic groups that leave their centre of mass stationary.

**Raman Applications: Anhydrous Cementitious Materials**

The main component of cement is called clinker and is obtained by firing raw materials (limestone, clay minerals, sand and iron minerals) at about 1500ºC in a rotary kiln. At this temperature a series of chemical reactions have been produced and nodules of clinker have been formed. Clinker is cooled, mixed with setting regulators (e.g., gypsum) ground to a fine powder and the mixture is called cement. Common phases in Portland cement clinkers are: alite (3CaO·SiO$_2$, C$_3$S$^1$), belite (2CaO·SiO$_2$, C$_2$S$^1$), tricalcium aluminate (3CaO·Al$_2$O$_3$, C$_3$A$^1$), and tetracalcium aluminate ferrite (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$, C$_4$AF$^1$). One typical composition of Portland cement consists of: C$_3$S = 55-60% (wt); C$_2$S = 15-20% (wt); C$_3$A = 5-10% (wt); C$_4$AF = 5-8% (wt) and CSH$_2$ = 2.6% (wt).

Silicate and aluminate structures have some problems to be studied by Raman scattering since they have very poor Raman scattering cross-section. The simplest method to achieving a useable signal-to-noise ratio is to use high incident powers. The second problem for Raman applications to cement is the presence of impurities, since cement has been prepared from quarry minerals with the impurity level close to 10%. The nature and amount of the impurities present in the cement sample can play an important role when choosing the wavelength to use. Synthetic silicates and aluminates phases have been used to identify Raman bands vibrations previous to studying the whole cement.

The FT-Raman spectra of synthetic silicate phases C$_2$S and C$_3$S obtained with 1064 nm, are with high fluorescence background. The spectrum of C$_2$S exhibits strong bands with maximums at 805 and 730cm$^{-1}$ due both of them to fluorescence. For the C$_3$S sample the Raman spectrum shows two peaks at 940 and 580 cm$^{-1}$ the width of the band depends on the spot size used. On the other hand FT-Raman of the synthetic C$_3$A compound shows less fluorescence and the Raman spectra exhibits two sharp bands at 760 and 510 cm$^{-1}$ that have been assigned to Raman scattering from Al-O stretching and bending vibrations respectively.

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$^1$ Cement chemistry nomenclature is used: C = CaO; S = SiO$_2$; A = Al$_2$O$_3$; F = Fe$_2$O$_3$; H = H$_2$O; $S$ = SO$_3$
For the anhydrous cement sample the FT-Raman presents three broad bands with maxima at 1400, 1000 and 650 cm\(^{-1}\) that are not the combination of the bands of synthetic C\(_3\)S, C\(_2\)S and C\(_3\)A phases. All these bands are due to fluorescence effects concealing the true Raman bands then 1064-nm line it is not appropriate to study anhydrous cement.

It is not completely clear the origin of the fluorescence of the cement in FT-Raman, some authors suggested that may be associated with the status of these compounds as orthosilicates. As we can see in the next section the fluorescence effect are progressively reduced on hydration.

Reproducible Raman spectra of the pure phases have been obtained with 514.5-, 632.8-, and 488-nm lines indicating that any of the three visible wavelengths seems to be appropriate for studying cements.

Figure 2 display Raman spectra of both pure calcium silicate phases C\(_3\)S and C\(_2\)S (laser 514 nm). The Raman spectrum of silicates is dominated by the internal modes of SiO\(_4\)\(^{4-}\) tetrahedral units with the symmetric and antisymmetric stretching of Si-O bonds within tetrahedral SiO\(_4\) groups, \(\nu_1\) and \(\nu_3\), situated at 777 and 935 cm\(^{-1}\) respectively. The symmetric and antisymmetric bending of the O-Si-O bonds, \(\nu_2\) and \(\nu_4\) respectively at 448 and 607 cm\(^{-1}\). The low wavenumber region (<300 cm\(^{-1}\)) correspond to the external lattice modes of the SiO\(_4\)\(^{4-}\) and Ca\(^{2+}\) ions.

![Raman spectra](image)

**Figure 2.** Raman spectra of pure C\(_3\)S and C\(_2\)S. * Satellite bands

Table I summarized the main Raman bands of the anhydrous cement phases. The various C\(_2\)S polymorphs can be identified by Raman. The low wavenumber region (<300 cm\(^{-1}\)) corresponds to the external lattice modes; for wavenumbers above 300 cm\(^{-1}\) the peaks arise from the internal modes of the SiO\(_4\)\(^{4-}\) groups that in the case of anhydrous phases correspond to Q\(^0\) tetrahedra. The wavenumber of the internal modes of C\(_2\)S and C\(_3\)S are far from the isolated, nondistorted SiO\(_4\)\(^{4-}\) (\(\nu_1\)–\(\nu_4\)) due to the high degree of distortion of the tetrahedral in the complex structure of these compounds.

The various C\(_2\)S polymorphs give characteristics Raman spectra. The most intense Raman band for, the thermodynamically stable phase at room temperature, \(\gamma\)-C\(_2\)S at around 813 cm\(^{-1}\) is characteristic of this phase and permits its identification. For this polymorph the second-most-intense band is positioned near 838 cm\(^{-1}\). The two more intense band of \(\beta\)-C\(_2\)S (metastable at room temperature) occurs at 977 cm\(^{-1}\) and 858 cm\(^{-1}\) and are both characteristics of this \(\beta\) phase. The other three polymorphs, \(\alpha\)'\(_L\), \(\alpha\)'\(_H\) and \(\alpha\), stable as pure C\(_2\)S only at
elevated temperatures can be stables at room conditions using stabilizers (B$_2$O$_3$ or BaO) producing broadness of the bands that it is more significant in the phases doped with B$_2$O$_3$. Another significant effect of the stabilizers is the shift of the position of the broad band. The Raman spectra of α and α phases are similar with the more intense band at ∼850 cm$^{-1}$ and another group of bands near 960, 530 and 400 cm$^{-1}$.

**Table I. Position (cm$^{-1}$) of the Raman peaks of the anhydrous phases**

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*Satellite band
If the synthesis procedure it is not CO$_2$ free some carbonation can be produce at the surface of the samples and peaks at 1084 cm$^{-1}$ ($\nu_1[\text{CO}_3^3]$); 715 cm$^{-1}$ ($\nu_4[\text{CO}_3^3]$) and 285 cm$^{-1}$ (Ca-O lattice vibrations) can be appears due to the presence of CO$_3^{2-}$ groups in calcite.

The C$_3$A-cubic polymorph spectra (Figure 3) displays a well-defined spectra with two dominant signals at 761 cm$^{-1}$ that corresponds to the stretching vibration of Al-O bond ($\nu_3[\text{AlO}_4^{5-}]$) and the line at 508 cm$^{-1}$ that corresponds to its deformation ($\nu_1[\text{AlO}_4^{5-}]$).

![Figure 3. Raman spectra of C$_3$A](image)

The C$_4$AF spectrum (Figure 4) is dominated by very high fluorescence emission that masks the Raman effect except for three broad bands with the following assignment, the signal at 736 cm$^{-1}$ is due to $\nu_1 [(\text{Fe,Al})\text{O}_4^{5-}]$ or $[(\text{Fe,Al})\text{O}_6^{9-}]$, the signal at 311 cm$^{-1}$ is attributed to $\nu_4 [(\text{Fe,Al})\text{O}_4^{5-}]$ or $[(\text{Fe,Al})\text{O}_6^{9-}]$ and the band at 258 cm$^{-1}$ is assigned to $\nu_2 [(\text{Fe,Al})\text{O}_4^{5-}]$ or $[(\text{Fe,Al})\text{O}_6^{9-}]$.

In real cement the main phases are alite (C$_3$S-base solid solutions i.e. MgO, Na$_2$O) and belite (C$_2$S-base solid solutions i.e.- Al$_2$O$_3$, Fe$_2$O$_3$). The presence of these impurities prompts a change in the crystalline structure of the silicate phases that may cause modifications in the Raman spectra. For the alite spectra a new line at 832 cm$^{-1}$ appears but for belite spectra a strong broadening of the silicate lines is observed.

Figure 5 present Raman spectra of both grey and white cement. It is possible to identify different vibrations bands from the calcium silicates, calcium aluminates, and gypsum, the last one added as setting regulator. Satellite bands from C$_3$S it is also observed.
Raman Spectroscopy: Application to Cementitious Systems.

Figure 4. Raman spectra of C_4AF

![Raman spectra of C_4AF](image)

Figure 5. Raman spectra of grey cement (Black line) and white cement (red line). * Satellite bands.

Raman spectra of gypsum shows four peaks due to SO_4 vibration modes: \( \nu_1 \) symmetric stretching (1006 cm\(^{-1}\)); \( \nu_2 \) symmetric bending vibrations (415 and 435 cm\(^{-1}\)); and two weak bands \( \nu_3 \) antisymmetric stretching vibrations (1135 cm\(^{-1}\)) and \( \nu_4 \) antisymmetric bending vibrations (620, 670 cm\(^{-1}\)). The presence of water in gypsum can be detected and characterized by peaks in spectral region near 3500 cm\(^{-1}\) and 1600 cm\(^{-1}\). In the high frequency Raman spectra, the peaks around 3500 cm\(^{-1}\) are caused by stretch vibration modes of water. In Mid-IR spectra, the peaks at 3395 cm\(^{-1}\) are \( \nu_1 \) symmetric stretch vibration modes of water, and the peaks at 3489 cm\(^{-1}\) are \( \nu_3 \) antisymmetric stretch vibration modes of water.

In the cement samples it is also observed a strong band at 1080 cm\(^{-1}\) due to calcium carbonate presence.

From the sustainability point of view new cement production has been developed in the past decades. One of these new cements is calcium sulphoaluminate (CSA) that was first
developed in China in the 1980’s. Industrial production requires essentially gypsum, bauxite and limestone as raw materials, which are burnt at 1,300°C in a conventional rotary kiln. These starting materials lead to a final clinker based on the quinary system CaO–SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$–SO$_3$ and formed by three main minerals: tetracalcium trialuminate sulphate (Ca$_4$A$_3$S); dicalcium silicate or belite (C$_3$S) and calcium sulphate or anhydrite (C$\delta$). Minor phases such as C$_3$A, C$_4$AF, C$_{12}$A$_7$ and (C$_2$AS) can also be present. Raman spectra of three main mineral phases of calcium sulfoaluminate cement and gypsum can be described as follow: i) C$_4$A$_3$S has two bands due to vibrational modes of sulphate [SO$_4^{2-}$] groups at 991 cm$^{-1}$ and 616 cm$^{-1}$, the third band at 521 cm$^{-1}$ is due to vibrational modes of [AlO$_4^{3-}$] tetrahedra in silicates; ii) belite spectra has been described previously; iii) Anhydrite shows a very strong band at 1018 cm$^{-1}$ ($v_1$ [SO$_4^{2-}$]) and minor signals at 1161 and 1130 cm$^{-1}$ ($v_3$ [SO$_4^{2-}$]), at 676, 627 and 609 cm$^{-1}$ ($v_4$ [SO$_4^{2-}$]) and at 499 and 417 cm$^{-1}$ ($v_2$ [SO$_4^{2-}$]); iv) gypsum as described above has a very intense band at 1006 cm$^{-1}$ ($v_1$ [SO$_4^{2-}$]) and minor peaks at 671 and 618 cm$^{-1}$ ($v_4$ [SO$_4^{2-}$]) and at 493 and 414 cm$^{-1}$ ($v_2$ [SO$_4^{2-}$]).

The Raman spectrum of the CSA cement presents the most intense bands located at 1016 and 991 cm$^{-1}$, in the region where stretching vibrations of [SO$_4^{2-}$] groups lie. On the basis of their frequencies they can be assigned to anhydrite and C$_4$A$_3$S, respectively. A broadened signal appears between 900 and 800 cm$^{-1}$, centered at 857 cm$^{-1}$. This feature is strongly asymmetrical: this is probably the result of the convolution of the two bands of C$_3$S, that appear unresolved or as a consequence of lower crystal perfection caused by the presence of foreign ions in the lattice or because of the small particle size of minerals of CSA clinker. The large band ranging from 750 to 550 cm$^{-1}$, because of the shape and the broadness, can be due to a fluorescence phenomenon occurring in presence of transition metals in the sample (Fe, Al). But it is also possible to highlight the presence of the three anhydrite bands at 676, 627 and 609 cm$^{-1}$, respectively. In the lower region of the spectrum a narrow and intense band appears at 418 cm$^{-1}$, together with a minor band at 500 cm$^{-1}$ and a broad band centered at 457 cm$^{-1}$ all of them arise from anhydrite.

**RAMAN APPLICATIONS: HYDRATED CEMENTITIOUS MATERIALS**

The cement hydration give rise both, amorphous phase calcium silicate hydrated (C-S-H gel) and two crystalline phases, portlandite and ettringite (Ca$_6$Al$_2$(OH)$_{12}$(SO$_4$)$_3$·26H$_2$O). C-S-H gel is the primary binding phase in Portland cement but poorly crystalline.

The *ettringite*, shows Raman bands from: i) OH at 3637 cm$^{-1}$ ($v_1$[OH]); ii) [SO$_4^{2-}$], $v_1$ at 989 cm$^{-1}$, $v_2$ at 450 cm$^{-1}$, $v_3$ at 1114 cm$^{-1}$ and $v_4$ at 605 cm$^{-1}$; iii) Al-(OH) stretch at 550 cm$^{-1}$.

C$_3$A and C$_4$AF hydrate very rapidly in the absence of sulphate, with the formation of a poorly crystalline gel that converts into a permeable network of needle-like hexagonal hydrates C$_4$AH$_{19}$ and C$_2$AH$_8$. As hydration proceeds, the hexagonal hydrates convert into the cubic hydrogarnet phase C$_3$AH$_6$. Gypsum addition prevent rapid hydration since ettringite is formed, upon hydration S/A ratio decreases and ettringite converts to monosulphoaluminate (Ca$_4$Al$_2$O$_6$(SO$_4$)$_3$·14H$_2$O, C$_6$A$\delta$H$_{14}$). The Raman spectra of these phase can be distinguished from *ettringite* since $v_1$ sulfate mode appears at 982 cm$^{-1}$ compared with 991 cm$^{-1}$ from ettringite. Water molecules are also present in $C_6$A$\delta$H$_{14}$, with water stretching vibration at 3688 cm$^{-1}$ almost 50 cm$^{-1}$ shift with respect to ettringite.
The other crystalline phase present in cement hydration, portlandite, Ca(OH)$_2$, shows two prominent sharp peaks, the first one at 3616 cm$^{-1}$ due to the presence of OH stretching and the second one at 353 cm$^{-1}$ assigned to Ca-O lattice vibrations.

While crystalline materials give sharp well-defined bands and the glasses give broad, poorly defined bands, the C-S-H samples lie between these two extremes. The distribution function, which describes the line shape of the bands, is strongly dependent upon the distribution of bond angles and bond lengths within common environments, and the broad half-width of the Raman bands of the C-S-H samples reflect their low symmetry and crystallinity. This distribution is assumed to be symmetry for glasses; hence, any asymmetry of the shape of the bands is due to a superimposition of several symmetrically shaped bands.

Raman spectra of synthetic C-S-H gel samples show a broad band in the 3800-3000 cm$^{-1}$ region attributed to OH stretching vibrations of water molecules. Depending on the C/S ratio of the C-S-H gel the frequency of the maximum can be different. The samples with C/S = 0.5 shows a main band at 3405 cm$^{-1}$. For samples with C/S > 0.5 shifts to higher frequencies, with a gradual shift to lower frequency with increasing C/S: 3480 cm$^{-1}$ for C/S = 0.67 and 3470 cm$^{-1}$ for C/S = 1.0. In some cases a band at 3565 cm$^{-1}$ appears and there are some discrepancies about the origin of this band, because of the possibility of Si-OH and Ca-OH presence. The broad band with maximum about 3240 cm$^{-1}$ is assigned to stretching motions of OH involved in a network of hydrogen bonds. The 1200-800 cm$^{-1}$ region encompasses Si-O silicate symmetrical stretching bands. The frequency of these bands increases with polymerization, thus, silicate units (Q$^3$) give rise to Raman bands at 1100-1050 cm$^{-1}$; chains (Q$^2$) at 1010-950 cm$^{-1}$; dimmer units (Q$^1$) at 900-870 cm$^{-1}$ and monomers (Q$^0$) at ~ 850 cm$^{-1}$. Internal deformations of the silicate tetrahedral of type $v_2$ and $v_4$ ([SiO$_4$]) generate bands in the regions 300-500 cm$^{-1}$ and 400-600 cm$^{-1}$ respectively. The band at 445 cm$^{-1}$ could be attributed to O-Si-O bending vibrations and the weak band at 490 cm$^{-1}$ may be due to antisymmetrical O-Si-O bending.

With respect to the calcium aluminate cement, the normal CAC hydration with water gives up to the development of hydrated calcium aluminates, CAH$_{10}$ at low temperatures but CAH$_8$ and C$_3$AH$_6$ at intermediate and high temperatures joint to AH$_3$ according to the following reactions:

1. CA + 10H $\rightarrow$ CAH$_{10}$ [1]
2. 2CA + 11H $\rightarrow$ C$_2$AH$_8$ + AH$_3$ [2]
3. 3CA + 12H $\rightarrow$ C$_3$AH$_6$ + 2AH$_3$ [3]

The C$_3$AH$_6$ and the gibbsite are the stable phases in this system. The $v_1$[AlO$_4$]$^3^-$ at 540 cm$^{-1}$ can be used to identify C$_3$AH$_6$ presence. Gibbsite ($Al(OH)_3$) shows four strong Raman bands at 3615; 3520; 3431 and 3361 cm$^{-1}$ assigned to OH stretching vibrations. The spectra also shows another three weak bands in the low-wavenumber region between 200 and 1200 cm$^{-1}$ consists of $\delta$(OH) and $\delta$(OH) modes, which involve AI-OH deformation, translation and Al–O–Al skeletal flexing vibrations. The 568 and 539 cm$^{-1}$ bands are attributed to Al–O–Al deformation and the 321 cm$^{-1}$ band with a shoulder at 306 cm$^{-1}$ is ascribed to Al–O stretching vibrations.
High early strength, good chemical resistance and high temperature resistance of calcium aluninate cement (CAC) products have encouraged the use of CAC in certain applications. However, conversion of hexagonal phases, CAH\textsubscript{10}, or C\textsubscript{2}AH\textsubscript{8} to cubic C\textsubscript{3}AH\textsubscript{6} and AH\textsubscript{3} in hydrated CAC cement under certain temperature conditions has been a major problem limiting its use. The presence of a minor amount of C\textsubscript{2}ASH\textsubscript{8} (strätlingite) in CAC at later ages may be responsible of the strength recovery after conversion. Strätlingite Raman have been recently determined with the main vibrations signals at 3692 and 531 cm\textsuperscript{-1}, the first one due to OH vibrations and the second one to four coordinated aluminium.

**Carbonated Compounds**

*Calcium carbonate* phases have been formed after portlandite carbonation, although vaterite is the least thermodynamically stable of the three crystalline calcium carbonate polymorphs, it is known for it to be formed upon carbonation of portlandite. Indeed, vaterite has been observed following exposure of C-S-H gels to carbon dioxide. The formation of vaterite may occur upon carbonation of pastes with high lime contents, and is favoured by the presence of imperfectly crystalline portlandite. The main vibration bands for calcium carbonate phases are: i) symmetric stretching \( \nu_1[\text{CO}_3] \); ii) split in-plane bending vibrations \( \nu_4[\text{CO}_3] \) and iii) Ca-O lattice vibrations. Depending on the calcium carbonate polymorph the vibration of the bands appears at different wavenumber that can be identified in Table II. Figure 6 shows a mixture of calcite, vaterite and aragonite with its identification.

![Figure 6. Calcite (C), vaterite (V) and aragonite (Ar) mixture.](image)

**Table II. Calcium carbonate polymorphs Raman bands**

<table>
<thead>
<tr>
<th></th>
<th>calcite</th>
<th>vaterite</th>
<th>aragonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>1080</td>
<td>1090, 1076</td>
<td>1080</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>712</td>
<td>740-750</td>
<td>701-704</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>282</td>
<td>268; 300</td>
<td>206</td>
</tr>
</tbody>
</table>
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Thaumasite \((\text{CaSO}_4 \cdot \text{CaSiO}_4 \cdot \text{CaCO}_3 \cdot 15\text{H}_2\text{O})\), a sulphate attack product, and ettringite \((3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O})\) structure are closely related, but Raman spectroscopy can be used to differentiate both compounds. The locations of the \(v_1\) \(\text{SO}_4\) peaks of both compounds overlap, but only the thaumasite shows the distinctive \(\text{Si}[\text{VI}]\) peak at 658 cm\(^{-1}\).

The main conclusion is the suitability of Raman spectroscopy to study fresh and hydrated cement minerals as well as its admixtures.

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