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Micro-Raman spectroscopy of thaumasite

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Abstract

Micro-Raman spectroscopy can be used to identify thaumasite. Three mineral samples were studied; in addition to the peaks at 658 and 990 cm^{-1} previously reported by Bensted and Varma (assigned to SiO_6 and SO_4 ν_1 stretching, respectively), further peaks were found, which we assign to carbonate (1072 cm^{-1}) and hydroxide/water (in the region of 3300 cm^{-1}) species. Thaumasite lost no water at 100°C even after prolonged heating, however, most of the water was lost after heating at 110°C for 10 min. Simultaneously, the sharp peaks due to sulfate and carbonate groups (990 and 1072 cm^{-1}) disappeared and were replaced by much broader peaks (1002 and 1082 cm^{-1}). However, for the peak at 658 cm^{-1} attributed to silicate, there was no clear replacement. Further changes were evident in the vibrations of sulfate species. Thaumasite in veins was readily distinguished from ettringite in two specimens of field concrete, based on the combination of peaks at 658, 990, and 1072 cm^{-1}, with spatial resolution of approximately 50 μm. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thaumasite; Spectroscopy; Raman; Ettringite; Durability

1. Introduction

Recently, there has been considerable interest in the thaumasite form of sulfate attack, and an expert group has reported in the UK [1]. In conventional sulfate attack, aluminates react to form gypsum and ettringite, with a potentially disruptive volume increase. In sulfate-resisting portland cements, the amount of aluminate and, thus, the potential for expansion, is strictly limited; the C-S-H gel is not affected by the reactions involving aluminates. In contrast, in the thaumasite form of sulfate attack (TSA), the C-S-H gel reacts with carbonate and sulphate ions to form thaumasite, and, thus, as well as some limited expansion, the C-S-H binding phase is consumed. Thaumasite is not a good binder, and the strength of the concrete is significantly reduced.

The structures of ettringite $C_3A\cdot 3C\bar{S}\cdot 31H$ and thaumasite $CS\cdot C\bar{S}\cdot C\bar{C}\cdot 15H$ are closely related, with both based on a cationic columnar structure, with anions between the columns [2]. Ettringite consists of columns of $[Ca_3(Al,Fe)(OH)_6\cdot 12H_2O]^{3+}$ with (generally) sulphate anions between the columns. Thaumasite consists of $[Ca_3Si(OH)_6\cdot 12H_2O]^{4+}$ columns with carbonate and sulfate ions between the columns. Hence, the unit cells and the diffraction patterns are also similar, particularly for the readily observed {100} and {110} reflections (at approximately 9° and 16° 2θ for $Cu_{K\alpha}$ radiation). Differentiation between the two is only possible with a high-resolution X-ray powder diffractometer. Higher-order peaks are better separated, but have an increased tendency for overlap with other peaks typically found in hydrated cement systems. Quantification of ettringite and thaumasite has been performed by X-ray powder diffraction [3], but is difficult. Ettringite is easily damaged during the grinding of samples to a fine powder for X-ray diffraction analysis.

Solid state ^{29}Si MAS NMR provides an excellent method for identification of thaumasite, since Si in octahedral coordination ($Si^{[6]}$) is well separated from Si in its normal tetrahedral coordination ($Si^{[4]}$); however, the equipment is not readily available, and quantification requires the use of special techniques [4] because of relaxation problems.

Peaks due to $Si^{[6]}$ are found in infrared spectra, but overlaps often occur and interpretation can be difficult without use of complex multivariate fitting models [5].

Raman spectroscopy is another technique that can be used to distinguish between $Si^{[6]}$ and $Si^{[4]}$ units. Bensted and Varma [6] obtained results from bulk Raman spectroscopy supporting the probable absence of $Si^{[4]}$ species in thaumasite shortly after the crystal structure was deter-

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mined. They assigned the peak at 658 cm^{-1} to Si$^{[6]}$. By today's standard, the spectra covered only a limited spectral range, and were extremely noisy due to limitations of the equipment available at that time. As far as we are aware, there have been no further reports of Raman spectroscopy of thaumasite. In Raman spectra of ettringite [7,8], no significant peaks were observed in the region below 950 cm^{-1}, allowing thaumasite and ettringite to be readily distinguished based on the thaumasite Si$^{[6]}$ peak at 658 cm^{-1}.

It is appropriate to consider why Raman spectroscopy of cement has been relatively limited. Cement samples tend to strongly absorb and fluoresce, swamping out the weak Raman signals, and forcing workers in this field to restrict their studies to pure calcium silicates and white cements [8]. Hopes that improved signals from cement samples could be obtained by means of lasers operating at different frequencies have been largely unsuccessful [9]. Use of a microprobe has given useful results [10], allowing signals to be obtained specifically from small regions of a sample. While in theory, for an ideal sample, this can be restricted to a few microns cubed; in practice for cements, we have observed signals from larger regions, as will be discussed below. Raman microprobe equipment is now more readily available, and techniques are available for obtaining continuous artefact free data over wide frequency ranges [11].

In this paper, these instrumental advances are used to reconsider the Raman spectroscopy of thaumasite. The original spectra are confirmed using a variety of crystalline mineral samples, and investigations are made of a series of cement and concrete samples including those previously studied using NMR by Skibsted et al. [4]. Additional peaks due to carbonate are assigned. Raman microprobe spectra are used to confirm the presence of thaumasite in a thin vein in a concrete studied by Yang and Buenfeld [12], where it would have been difficult to perform XRD studies due to the presence of only very small amounts of material.

It is hoped that these results will lead to use of the technique for diagnosis of thaumasite formation in deteriorated structures. While the equipment is relatively expensive, spectra can be obtained rapidly, and extensive sample preparation is not needed, with either powders or polished sections (not resin impregnated) being suitable for study.

2. Experimental

A range of thaumasite samples from mineral deposits and cements were studied. A pure mineral sample (B1) from Crestmore, CA, and a sample of deteriorated concrete (B2) from the Tredington Ashchurch M5 motorway overbridge (UK) were kindly supplied by Dr. N. Crammond of BRE. A sample of concrete from a tunnel lining (Y1) was obtained from Drs. N. Buenfeld and R. Yang, which they had previously studied using low-vacuum SEM [11]. Dr. J. Skibsted of the University of Aarhus kindly supplied samples from his extensive NMR study [4], and we adopt his numbering here with addition of a prefix S. Full details of these samples are given in his paper [4], but S1 and S2 are mineral samples from Sulitjelima, Sweden and NJ, USA, respectively, while S3–S7 are various synthetic laboratory samples containing 3–15% thaumasite along with various silicate, sulfate, and carbonate containing reagents. The synthetic samples had been stored dry for upwards of 5 years, and after receipt at Imperial College, were stored wet at 5°C for a week prior to study to counter any possible dehydration and consequent loss of crystallinity.

Raman spectra were acquired using a Raman microprobe (Renishaw system 2000) equipped with lasers with frequencies of 633, 520, and 488 cm^{-1}. Typically, 25 mW was present at the laser and gave 5 mW at the microscope objective. The variable temperature stage used contained the sample in a partially enclosed chamber, mounted on a temperature controlled metal block.

3. Results

Spectra of the minerals are shown in Fig. 1(a). For samples B1, S1 and S2, clear peaks can be observed, both for the OH/

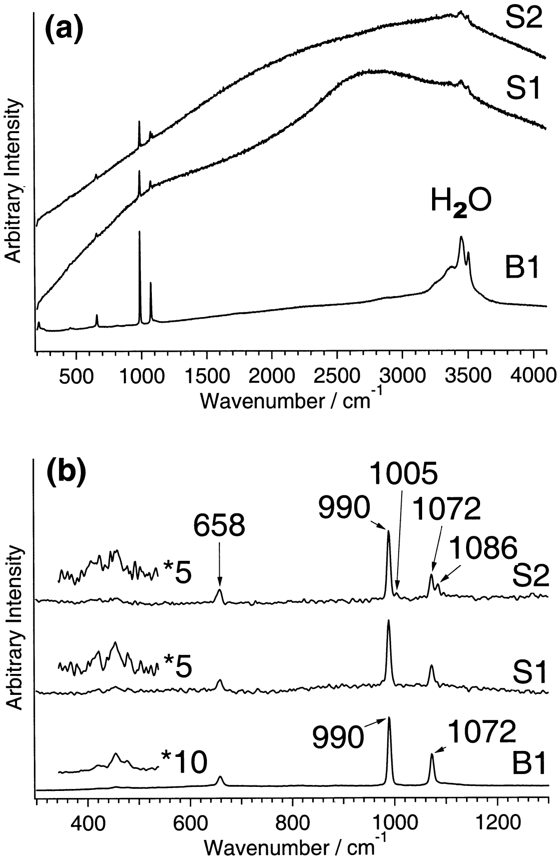

Fig. 1. Micro-Raman spectra for the mineral samples of thaumasite B1, S1, and S2: (a) raw spectra as obtained; (b) expansion of the region from 300 to 1300 cm^{-1} after stripping out the broad fluorescence background.

water region around 3300 cm^{-1} and in the region < 1500 cm^{-1} despite the substantial fluorescence, which also takes place. After baseline stripping of this fluorescence from the region < 1500 cm^{-1}, good spectra were obtained as shown in Fig. 1(b). Peaks at 658 and 990 were assigned on the basis of the literature [6] to $Si^{[6]}$ and sulfate groups, respectively. The peak at 1072 cm^{-1} was assigned to carbonate based on the nearby literature values for carbonates in other phases. In addition, three weak peaks in the region 400–500 cm^{-1} were also observed, probably due to other sulfate vibrations. For sample S2, which contained traces of $CaCO_3$, an additional peak at 1086 cm^{-1} was assigned to carbonate groups in calcite. For sample B1, which has the best baseline, a broad peak in the region of 1100 cm^{-1} could also be observed perhaps due to sulfate ν_2 vibrations.

On heating a small fragment of sample B1, the spectra were essentially unchanged below 110°C, but on heating at 110°C hydroxyls, water and the peak due to $Si^{[6]}$ species are lost over a period of about 10 min (Fig. 2(a)). This is consistent with the dehydration behaviour reported previously [6]. Simultaneously, as shown in the baseline-corrected expansions in Fig. 2(b), the peaks due to carbonate and sulfate are shifted to higher wavenumbers and broadened, as are the low-frequency weaker peaks. Further heating to 120°C completes the process. No further changes were observed on heating to 300°C.

In the polished samples, Y1, containing localised bands of thaumasite previously studied by Yang and Buenfeld [12], Raman microprobe spectroscopy easily distinguished between thaumasite and ettringite (Fig. 3). While the samples were embedded in resin, resin signals were not observed from the regions studied. The locations of the SO_4 ν_1 peaks overlap, but only the thaumasite bands show the distinctive $Si^{[6]}$ ν_1 peak at 658 cm^{-1}. Note also that the thaumasite peaks are quite sharp, while the ettringite peaks are significantly broadened, presumably because some water has been lost in specimen preparation. For some of the narrower bands, peaks from surrounding material (in this case quartz) appear in the spectra, indicating that the analysed zone is at least the width of the band.

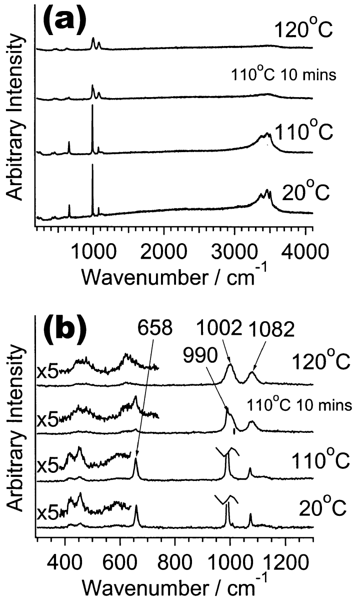

Fig. 2. Micro-Raman spectra showing the dehydration of a small grain of mineral thaumasite sample B1: (a) raw spectra as obtained; (b) expansion of the region from 300 to 1300 cm^{-1} after stripping out the broad fluorescence background. In (b), the peaks at 1002 cm^{-1} have been cut short to allow the four spectra to be plotted with the same (arbitrary) vertical scale; (a) shows the full peak heights.

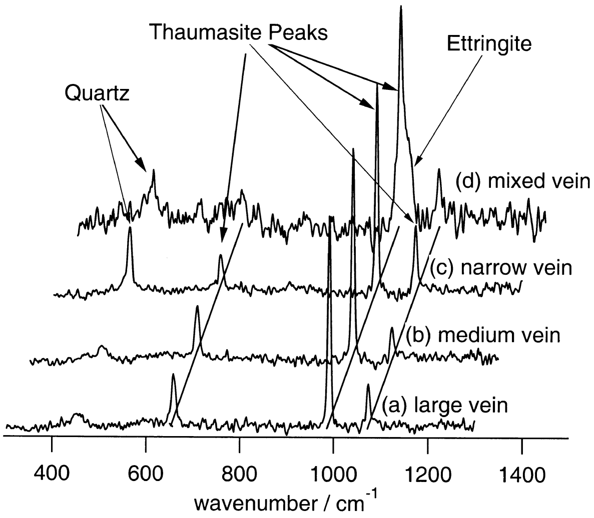

Fig. 3. Micro-Raman spectra from different regions of sample Y1 after background subtraction. (a–c) Signals from thaumasite rims of varying thickness. (d) Signal from a mixed thaumasite/ettringite region. Plots are offset successively by 50 cm^{-1}.

In the samples containing thaumasite formed from TSA on concrete, mortar or cement paste, the thaumasite is spread throughout the areas previously containing C-S-

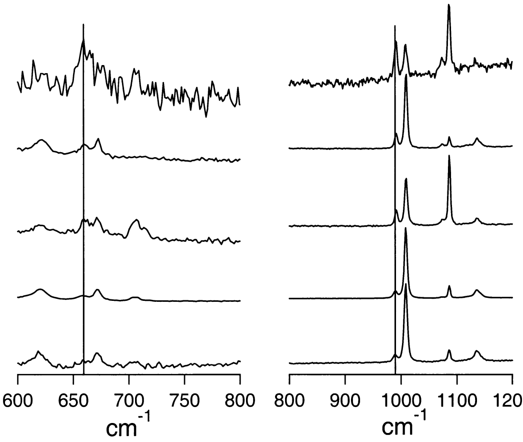

Fig. 4. Micro-Raman spectra of samples S3 (bottom two traces) and S4 (top three traces) showing peaks due to thaumasite (marked by vertical lines) and other peaks due to the other materials present, such as gypsum, lime and calcite. All spectra are baseline corrected to remove the broad signals due to fluorescence.

H gel rather than forming distinct bands. Analyses of these samples, S3–S7 and B2, by Raman microprobe spectroscopy were largely unsuccessful in locating thaumasite, except for the samples (S3 and S4) made from pure phases and containing the highest levels of thaumasite along with low levels of impurities such as Fe (Fig. 4). In these samples, thaumasite peaks could just be observed. In the samples based on real cements, however, no peaks could be observed, and much fluorescence occurred. It appears that unless thaumasite is present in very high levels, the thaumasite Raman signal is too weak to observe in complex matrices.

4. Discussion

The presence of signal from the surrounding quartz aggregate when the narrow bands in sample Y1 were investigated indicates that the Raman microprobe was analysing quite a large volume, of the order of a 50 μm cube, which is much less localised than the ultimate resolution of a 2 μm cube for the Raman equipment and the lens used [13]. It would appear that signal is being observed from below the focus of the beam at the surface of the material, due to its low optical absorption.

This may account for the difficulty of observing low levels of thaumasite from within a mixed matrix. The other material present in the matrix absorbs strongly, limiting the volume from which Raman signal is observed, and, hence, the magnitude of that signal. High levels of fluorescence from the rest of the matrix make it harder to observe a small signal. In addition, finely divided material may also be poorly crystalline and give less sharply defined peaks in the Raman spectrum.

Bensted [14] also notes that laser Raman spectroscopy can be useful for screening white deposits associated with deteriorated concrete to see whether any sulfate attack was of the normal (ettrigite) variety, or involved thaumasite formation. The technique was cost-effective, since it was possible simultaneously to screen for alkali silica reaction.

5. Conclusions

The Raman microprobe technique is rapid and unequivocal for identification of veins of thaumasite. Strong fluorescence could be removed by background subtraction techniques. The technique was also useful for following dehydration of ettringite on heating. The low spatial resolution meant the technique was not suitable, however, for diagnosis of TSA where bulk conversion has occurred and the products are finely divided and intermixed with the other minor elements from cement hydration.

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