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Discussion

# A discussion of the paper "Micro-Raman spectroscopy of thaumasite" by A.R. Brough and A. Atkinson[☆]

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Dr. Brough and Prof. Atkinson have clearly demonstrated the value of the Raman microprobe technique for rapidly and unequivocally identifying veins of thaumasite from mineral deposits and cements subjected to sulphate attack. This was aided by background subtraction techniques to remove the strong fluorescence observed. The low spatial resolution meant that the use of micro-Raman spectroscopy did not prove to be suitable for the diagnosis of thaumasite sulphate attack (TSA), where bulk conversion had arisen and the products were finely divided and intermixed with the other minor elements from cement hydration [1].

However, it is actually possible to diagnose TSA by carefully removing the white deposits observed and examining these by Raman spectroscopic techniques [2]. As the authors mention in their paper [1], laser Raman spectroscopy can be useful for screening white deposits associated with deteriorated concrete to see whether any sulphate attack is of the normal (ettringite) variety or has involved thaumasite formation (TF) [3].

The problem that Brough and Atkinson experienced in only identifying thaumasite in real cement samples when very high levels of this deterioration product are experienced [1] can be ascribed to the relatively weak Raman signals emanating from the $[Si(OH)_6]^{2-}$ groups present in thaumasite. The Raman spectral peaks for silicate indicate, from their relatively low intensity and somewhat squat nature, that the $[Si(OH)_6]^{2-}$ octahedra are degenerate and hence very much distorted away from the ideal $O_h$ symmetry expected for regular octahedra. This would be expected from the observations that special conditions are necessary for permitting the stable existence of the $[Si(OH)_6]^{2-}$ groups, such as charge delocalisation from the small strongly polarising $Si^{4+}$ cations onto other neighbouring groups present within the thaumasite structure like the square planar carbonate $CO_3^{2-}$ groups. This would agree with the situation that occurs at ca. 110 °C when decomposition to the disordered structure thaumasite glass takes place alongside the loss of water, which begins at this temperature when the randomly distributed silicate groups assume the normally encountered 4-coordination of silicon by oxygen in the tetrahedral $SiO_4^{4-}$ ions under the prevailing conditions [4–7].

The authors also found micro-Raman spectroscopy to be a useful technique for examining the composition of thaumasite, which has a greater range of temperature stability than ettringite, where lattice collapse is commonly encountered above ca. 50–60 °C, often depending upon the length of time the ettringite is maintained at these temperatures. No water loss was found for thaumasite at 100 °C, even after prolonged heating. The lack of any lattice collapse in thaumasite prior to decomposition is an indication that the $H_2O$ content is more strongly bound than in ettringite, even though both structures exhibit a hexagonal-type prism morphology. This state of affairs is undoubtedly due, at least in part, to the stabilising effects of the charge delocalisation of the highly polarising $Si^{4+}$ cations in thaumasite.

The aforementioned behaviour is clearly demonstrated by micro-Raman spectroscopy from the results of the heating up of thaumasite [1]. The disappearance of the main $\nu_1$ peak of the $[Si(OH)_6]^{2-}$ configuration, accelerating when thaumasite is heated at 120 °C in comparison with its being heated at 110 °C, is a manifestation of the lack of stability for Si(VI) to endure when the thaumasite structure decomposes to a randomly distributed arrangement of ions within the thaumasite glass being formed.

Woodfordite, which is a solid solution between ettringite and thaumasite, does not appear so far to have been studied by Raman spectroscopic techniques. This solid solution is not total, as has been found experimentally and also in nature where sometimes thaumasite exists as overgrowths on ettringite and vice versa. Crystallographic examinations of ettringite–thaumasite solid solutions [8] have revealed a likely discontinuity in the solid solution between them, which is characterised by a gap in the a axis dimensions at

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ca. 11.11 – 11.17 Å. This suggests that an unstable range of compositions within the solid solution series could exist in practice. Micro-Raman spectroscopic investigations could be usefully applied here to back up the aforementioned crystallographic work.

Thus the micro-Raman spectroscopic study of thaumasite undertaken by Brough and Atkinson [1] has indeed been usefully employed for identifying thaumasite and also for readily distinguishing between ettringite and thaumasite in veins of field concrete, in addition to shedding more light upon the nature of thaumasite. This is especially important in view of the increased usage now of Portland limestone cement compositions and limestone additions to Portland cements as fillers in standards like EN 197-1 [9] and BS 7979 [10]. Here there needs to be increased awareness of the potential for TSA to occur at temperatures below 15 °C in situations where sulphate attack can arise [11 – 15]. Adequate precautions need to be taken in terms of judicious choice of cement type and possible admixture usage in order to prevent, or at least minimise, the risk of potential TSA damage from any such occurrences in likely sulphated environments [5,11 – 15].

However, it should not be forgotten that the mere appearance of small specks of thaumasite upon mortar or concrete structures is not per se an indication of distress within structures. The Thaumasite Expert Group report [12] covers this aspect in its differentiation between TF and TSA. Although what appears to be TF may sometimes be the onset of TSA, this particular aspect can be dealt with by regular inspection of the structures concerned to see whether any distress to the structures concerned does appear in the fullness of time. Should such distress occur then the necessary remedial measures can be taken [12].

Overall, the simple but straightforward micro-Raman spectral investigation undertaken by the authors [1] is a valuable contribution towards our further understanding of the precise nature of thaumasite.

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