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Conference paper

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Hydrate Characterisation

Raman Spectroscopy for the Analysis of Cements – Past, Present and Future

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Until recently there has been a common held misconception that Raman spectroscopy of cements is not possible, or at least so inconvenient as to make it impracticable. However, whilst not a routine analysis method Raman analysis of cementitious materials is possible, provided that suitable consideration is given to the technique's limitations. This paper will chart the history of Raman spectroscopy applied to cementitious systems, review recent developments in the field and look towards possible future developments. Raman spectroscopy is a vibrational spectroscopic technique often considered complementary to infra-red spectroscopy, and provides information on the short-range order and local bonding in materials. Furthermore, the common coupling of a spectrometer to an optical microscope enables spatial resolution in the order of microns, whilst the rapid analysis times and low sensitivity towards water enables in-situ analysis of hydrating pastes. Furthermore, the technique is particularly sensitive to sulphate and carbonate environments, and is semi-quantitative.

The earliest application of Raman spectroscopy applied to cements was that of Bensted¹ who was able to obtain spectra from WPC and clinker standards but whose OPC spectra were plagued by fluorescence, a limitation which has hindered the widespread application of the technique. This was compounded by other earlier studies which used the standard approach to overcoming fluorescence^{2, 3}, i.e. using a longer wavelength laser, e.g. (1064 or 785 nm). However, the intense, broad bands seen when using NIR or IR excitation sources are photoluminescence bands due to the presence of trace impurities⁴, most probably rare earth elements, within the cement mineral lattice.

Early studies also struggled with poor scattered light collection, necessitating long collection times and poor spectral resolution. However, with improved technology leading to better light collection, analysis times have fallen and spectral quality improved. Consequently in recent years there has been a resurgent interest in the application of Raman spectroscopy for analysis of cements.

The spectra of the principal components of anhydrous cement have been oft reported, with the technique not only, for example, being able to distinguish alite from belite, but also different polymorphs of each phase. More recently, coupling of a spectrometer with a low vacuum SEM has enabled simultaneous Raman, elemental and morphological analysis⁵. This has enabled a more detailed examination of the interstitial aluminate, ferrite and sulphate phases.

The low sensitivity towards water, plus the ability to readily differentiate the different anhydrous phases has prompted numerous studies using Raman spectroscopy to follow hydration, both of pure clinker phases⁶⁻⁹ and of cements^{10, 11}. The ability to characterise poorly ordered materials has also led to the technique's application for the characterisation of C-S-H phases, not only in the aforementioned hydration studies, but also for systematic structural studies¹²⁻¹⁴. Differences in silicate structure could readily be distinguished, and by comparison with crystalline C-S-H phases¹³ structural information could be ascertained. These studies also took advantage of the aforementioned sensitivity towards carbonate by following the carbonation of the phases during their first few hours of exposure to air¹⁴ revealing the formation of amorphous calcium carbonate as a crystalline carbonate precursor.

Just as the technique is sensitive towards the carbonate local environment, it is similarly sensitive towards sulphate (and indeed any symmetrical anion), which has proved incredibly useful. The consumption of gypsum and its conversion to ettringite and then monosulphate upon cement hydration has been reported on many occasions^{6, 7, 10, 11}. However, it was Raman spectroscopy's role in the determination of the structure of thaumasite which deserves mention. Whilst XRD and SEM-EDX both struggle to identify thaumasite intermixed with ettringite, Raman spectroscopy has no such difficulty thanks to the presence of six-fold coordinated silicon giving rise to a characteristic bands at 663, 431, 258 and 219 cm^{-1} ¹⁵. In addition to this recent work on Portland-based systems, there has also been research into lime mortars¹⁶⁻¹⁹, sulphoaluminate²⁰ and Sorel cements²¹.

So, what about the future? The chief problem remains obtaining good quality spectra from OPC, and whilst OPC clinker has been analysed, good quality spectra from OPC especially when hydrated have proved elusive. If a solution could be found to this problem then there would be an even greater resurgence in the use of the technique. A possible solution will be suggested in the presentation.

The next possible advance would be real-time hydration studies, necessitating improvements in Raman signal collection and detector efficiency. Given the ever improving technical specifications of the latest spectrometers, such real-time studies may not be far away. Allied to this would be the capabilities to perform real-time imaging of heterogeneous samples, most likely pastes, to investigate the spatial relationship between the different phases. This will also entail the development of techniques for data processing to extract information from complex heterogeneous systems. This will also be discussed in the presentation.

In summary Raman spectroscopy of cements is possible, and has an important role to play in the field. This presentation will hopefully show some of the possibilities and provide pointers for future research.

References

1. J. Bensted, *J. Am. Ceram. Soc.*, 1976, **59**, 140.
2. D. Bonen *et al.*, *Cem. Conc. Res.*, 1994, **24**, 959.
3. C. D. Dyer *et al.* *Spectrochim. Acta A -Mol. Biomol. Spec.*, 1993, **49**, 715.
4. C. Dyer and B. J. E. Smith, *J. Raman Spec.*, 1995, **26**, 777.
5. L. Black and A. Brooker, *Adv. App. Ceram.*, 2007, **106**, 327.
6. L. Black *et al.*, *J. Mater. Chem.*, 2006, **16**, 1263.
7. L. Black *et al.*, *Adv. App. Ceram.*, 2006, **105**, 209.
8. J. Ibanez *et al.*, *J. Raman Spec.*, 2007, **38**, 61.
9. M. Tarrida *et al.*, *Adv. Cem. Based Materials*, 1995, **2**, 15.
10. C.-S. Deng *et al.*, *Journal of Materials Chemistry*, 2002, **12**, 3105.
11. S. Martinez-Ramirez *et al.*, *J. Raman Spec.*, 2006, **37**, 555.
12. K. Garbev *et al.*, *Journal of the American Ceramic Society*, 2007, **90**, 900.
13. R. J. Kirkpatrick *et al.*, *Advanced Cement Based Materials*, 1997, **5**, 93.
14. L. Black *et al.*, *Journal of the American Ceramic Society*, 2007, **90**, 908.
15. S. P. Varma and J. Bensted, *Silicates Industriels*, 1973, **38**, 29.
16. D. D. Edwards *et al.*, *Adv. App. Ceram.*, 2007, **106**, 309.
17. A. El-Turki *et al.*, *Heritage, Weathering and Conservation*, 2006, **1-2**, 51.
18. A. El-Turki *et al.*, *Cement and Concrete Research*, 2007, **37**, 1233.
19. S. Martinez-Ramirez *et al.*, *Cement and Concrete Research*, 2003, **33**, 2063.
20. D. Gastaldi *et al.*, *Journal of Materials Science*, 2007, **42**, 8426.
21. I. Kanesaka and S. Aoyama, *J. Raman Spec.* 2001, **32**, 361.