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RAMAN SPECTROSCOPY OF CEMENTS: PROBLEMS AND POSSIBILITIES

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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. With recent advances in Raman spectrometers resulting in more efficient spectrometers, faster acquisition times and the use of lower powered lasers there has been a resurgence in the application of the technique to the study of cementitious materials. However, there are limitations, ready to catch the inexperienced user unawares. Fortunately, by understanding the technique's limitations and the origin of some of the likely problems, it is possible to obtain valuable information from cementitious systems, gleaning information for example on chemical structure, hydration reactions, or early stage carbonation. This paper will show the development of Raman spectroscopy applied to cementitious systems, review recent advances in the field and look towards possible future applications.

Some of the earliest work in the field was by Bensted who was able to obtain spectra from white Portland cement (WPC) and clinker standards but whose spectra from ordinary Portland cement (OPC) were swamped by a fluorescent background signal (Bensted 1976). More than any other factor it is fluorescence which has hindered the widespread application of Raman spectroscopy in cement science (Dyer *et al.* 1993; Bonen *et al.* 1994). This problem was compounded by early studies which used the standard approach to overcoming fluorescence, i.e. using a longer wavelength laser, e.g. (1064 or 785 nm). In these studies, the intense, broad bands seen when using NIR or IR excitation sources were photoluminescence bands due to the presence of trace impurities (Dyer and Smith 1995), most probably rare earth elements, within the cement mineral lattice. However, by avoiding wavelengths greater than ~ 700 nm it is possible to obtain good quality spectra from many cementitious materials. Figure 1 demonstrates shows the Raman spectra obtained from Portland cement clinker using 633 and 785 nm laser excitation (left), plus spectra obtained from synthetic principal clinker phases (right).

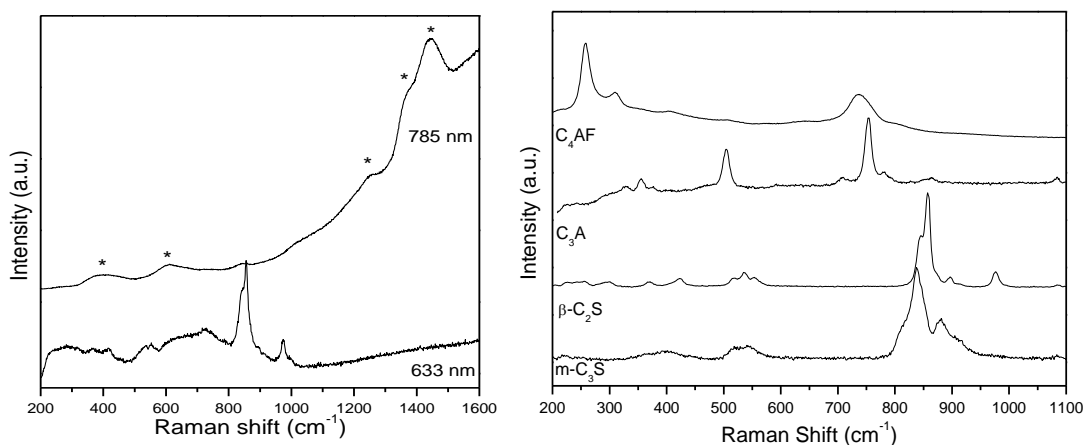


Figure 1: (left) Raman spectra recorded from an OPC clinker nodule under 633 and 785 nm excitation and (right) spectra obtained from synthetic clinker minerals.

Furthermore, the sensitivity of Raman spectroscopy towards water is very low, and there have been a number of studies looking at the hydration of both clinker standards, i.e. monoclinic C_3S , C_2S , C_3A and C_4AF , (Black *et al.* 2006 a,b; Ibanez *et al.* 2007) and cements, including white Portland cement and Oilwell cement (Deng *et al.* 2002; Martinez-Ramirez *et al.* 2006). However, the ultimate goal would be characterisation of hydrated OPC, but this has remained elusive; an elusiveness extending to OPC *per se*, where spectra are plagued by prohibitively high background signals. This was assumed to be due to the high iron levels in OPC, explaining the ability to obtain spectra from WPC. However, spectra obtained from a Class G oilwell cement containing almost 19% ferrite and characterisation of an OPC clinker nodule disproved this. More likely, grinding leads to a high background signal through the introduction of defects or by increased inter-particle scattering. Figure 2

shows spectra from an OPC clinker nodule before and after grinding, plus that recorded from bagged, ground clinker. Grinding increased the background signal, but the effect diminished upon photobleaching, the process of leaving a sample under the laser beam for some time prior to analysis. Grinding the clinker introduced defects into the sample, leading to fluorescence. Some of these defects were annealed during photobleaching and the background diminished, but did not revert back to its original level. The increased background seen after photobleaching was due to inter-particle scattering. However, these explanations alone could not explain the prohibitively high background signal seen in the spectra of anhydrous bagged, ground OPC (figure 3a). Whilst photobleaching reduced the background signal slightly (3b), it was found that washing the clinker in organic solvents reduced the background dramatically (3c), and then yet further by subsequent photobleaching (3d). This indicates that the primary cause of fluorescence in OPC spectra is organic contamination, with further increases in the background signal is attributed to defects introduced during grinding, which can be partly removed by photobleaching. However, there remains a stubbornly high background signal, due to inter-particle scattering. This signal can be partly removed by using a low fluorescence, high refractive index immersion oil (3e).

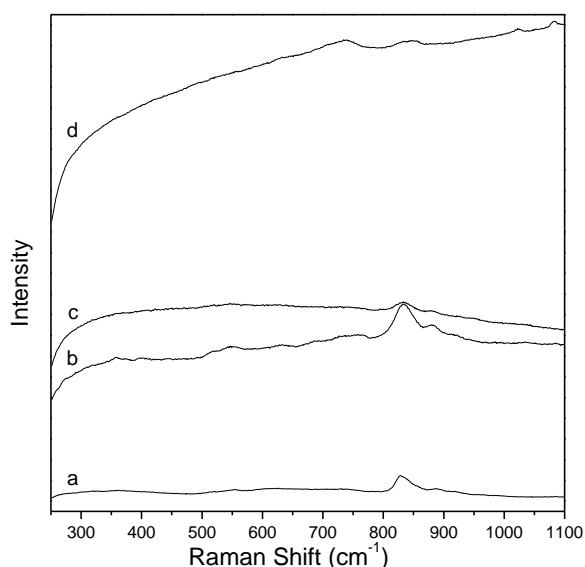


Figure 2: Spectra from anhydrous OPC clinker. a) nodule, b) ground and then photobleached for 5 minutes, c) ground nodule d) commercial ground and bagged OPC clinker.

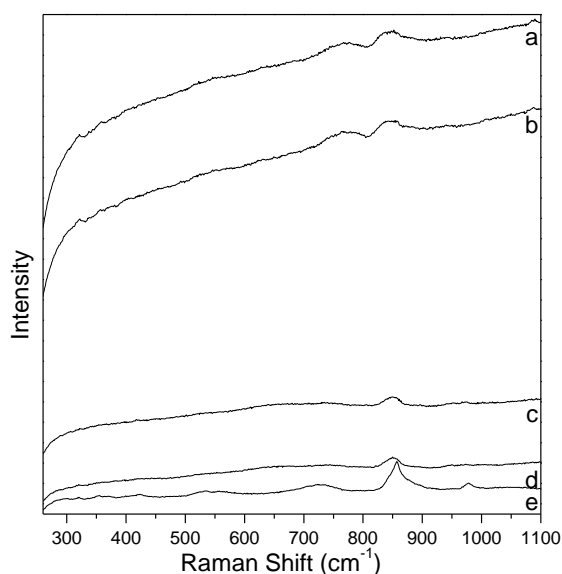


Figure 3: Spectra from commercial clinker. a) as received, b) photobleached for 5 minutes, c) solvent washed, d) as c after photobleaching, and e) as d but using an immersion oil.

These results show that OPC analysis is hindered by many factors, but that removal of organic material is necessary for good quality Raman spectra. However, in doing so, trace constituents such as grinding aids will be removed, which may affect the hydration behaviour of the cement. It therefore appears that Raman spectroscopy will be limited to studies of non-OPC system, for example lime mortars, calcium sulphoaluminate systems, calcium aluminate systems, geopolymers, etc. Other possible developments may involve the coupling of spectrometers with other instruments, such as electron microscopes, or in the development of chemometric approaches to process very large numbers of spectra from such heterogeneous systems. However, it is likely that Raman spectroscopy will remain a niche technique finding application in very specialised circumstances.

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