Available online at www.sciencedirect.com
SCIENCE DIRECT®
Cement and Concrete Research 36 (2006) 656 – 662
Cement and Concrete Research

The application of Raman spectrometry to investigate and characterize cement, Part I: A review

S.S. Potgieter-Vermaak [a,*], J.H. Potgieter [b], R. Van Grieken [a]

[a] Department of Chemistry, University of Antwerp, Universiteitsplein 1, B 2610 Antwerp, Belgium
[b] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag X3, Wits, 2050, South Africa

Received 21 March 2005; accepted 21 September 2005

Abstract

Raman spectrometry has received attention for the past 3 decades in its application to the characterisation of pure cement phases, white and grey cements. Various configurations of instrumentation and laser excitation sources have been used, as reported in a limited number of papers. The first demonstrated investigation in 1976 by Bensted, illustrated the characterisation of various pure mineral cement phases with the use of a visible excitation source and a standard dispersive configuration. This was soon followed by an investigation of pure phases, as well as white and grey cements in 1980 by Conjeaud and co-workers using a microprobe configuration and visible excitation. Considerable difficulties with excessive fluorescence phenomena, especially with grey cements, have however been reported from the initial to the most recent publication. This review aimed to report on Raman studies of pure synthesized cement phases, cement phases as found in white and grey cements, various forms of gypsum and related compounds as found in cement and concrete, hydration of pure cement phases, as well as those of white and grey cement and lastly carbonation effects. Results reported are discussed and tables of summarized observed Raman shifts are given.

Keywords: Hydration; Spectroscopy; Characterisation; Cement; Raman spectrometry

1. Introduction

The use of Raman spectrometry in the characterisation of the various cement and secondary cementitious materials (SCMs) has been investigated intermittently over the last 3 decades. In contrast to the application of Infrared Spectroscopy (IR), which has been well established as a technique to identify and estimate the various cement phases, the successful application of Raman spectrometry in cement and SCMs is still under investigation and discussion. The potential of Raman spectrometry for the characterisation of cement minerals was first demonstrated by Bensted [1] in 1976 and a critical examination of the limiting fluorescence phenomena of cement is currently in press [2]. The growth of the analytical applications, in general, of Raman spectrometry over the last 70 years has been spectacular, with capabilities of performing conventional analytical determinations and complex measurement tasks. Raman spectrometry can take advantage of the convenience of a range of instrumental configurations, from dispersive to interferometric systems, from monochannel to multichannel detection schemes, and a wide choice of laser systems for convenience of excitation and filter units for spectral purification. The further development and improved configuration of the micro-Raman instrument enable investigations at the micrometre level and provide spectral resolutions of up to 1 cm^{-1}. It can be considered as one of the most powerful, versatile and fascinating tools for the investigation of matter and it is therefore not surprising that a continued attempt is made to use it as an analysing and characterising tool for cement and SCMs. Two review articles were found concerning the application of Raman spectroscopy to the characterisation and hydration behaviour of cement and SCMs [3,4]. The first was written in 1980 and reported mainly on infrared spectrometry studies. The only Raman studies reported in this paper were that of the pioneer Bensted [1] and the article published by Conjeaud and Boyer in 1980 [5]. The second review by Bensted was written in 1999 and included results

---

* Corresponding author. Permanently employed by the Department of Chemistry and Physics, Tshwane University of Technology, Pretoria, South Africa.

E-mail address: sanja.potgieter@ua.ac.be (S.S. Potgieter-Vermaak).

0008-8846/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2005.09.008

obtained by other authors too [5–8]. This review aims to give a comprehensive summary of what has been investigated and published up to the end of 2004. The results that were obtained will be critically reviewed.

2. Characterisation of gypsum and its derivatives

Gypsum is one of the simplest components in the cement system and can be present in the dihydrate, hemihydrate or anhydrite form. Its identification and characterisation in a mixture with cement clinker are of importance for the hydration behaviour of cement and in the analysis of concrete undergoing external sulphate attack, e.g. when sulphate bearing water causes various surface chemical alterations. The main sulphate bearing products of interest in the cement, hydrated cement and degraded cement are calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$), ettringite ($6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$) and thaumasite ($CaCO_3 \cdot CaSO_4 \cdot CaSiO_3 \cdot 15H_2O$). The pioneer in Raman studies on cements and SCMs, Bensted [1], was of course the first to report on a hydration study and subsequent identification of the various forms of gypsum. A summary of the findings of all the papers cited in this article [1,4,9,10] is given in Table 1. Bensted found that the different gypsum forms differed distinctly in their Raman fingerprint, even at the strongest inelastic scattering, which is assigned to the totally symmetric sulphate stretching mode. This enables not only a relatively easy characterisation of the specific form of gypsum, but also the possibility to study the different hydration behaviours. Bensted reported in a dedicated paper [9] that the distinct advantage of Raman spectroscopy over that of IR spectroscopy is that water is a good Raman solvent and therefore hydration can be studied without interference. Furthermore, the well resolved bands can be used for quantitative phase analysis. He proposed in a review paper [4] that the false set of white Portland cements could be prevented by examining the hydration state of the gypsum. The most recent paper on gypsum involves an in situ investigation of the dehydration mechanism in natural gypsum [10]. The relevant Raman shifts are reported in Table 1.

Table 1
Summary of the observed Raman shifts for various forms of gypsum using different excitation sources

Ref.	Conditions	Raman shift (cm^{-1})				
		$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot$ ½H_2O	$CaSO_4$ soluble	$CaSO_4$ insoluble	Assignment
1	632 nm	414 mw	438 mw	438 mw	420 mw	ν_2 SO_4
		494 mw	494 mw	498 mw	500 mw	
		622 w	602 w	604 w	611 w	ν_4 SO_4
		624 w	636 w	624 w	630 w	
		676 w	676 w	678 w	679 w	
		1010 vs	1018 vs	1020 vs	1022 vs	ν_1 SO_4
		1114 w	1132 w	1131 w	1116 w	ν_3 SO_4
		1138 w	1150 w	1150 w	1134 w	
		1144 w	1174 w	1172 w	1166 w	
10	514 nm	420 mw	421 mw	424 mw		ν_2 SO_4
		494 mw	490 mw	490 mw		
		623 w	630 w	608 w		
			680 w	628 w		ν_4 SO_4
				668 w		
				685 w		
		1008 vs	1014 vs	1026 vs		ν_1 SO_4
		1114 w	1152 w	1105 wbr		ν_3 SO_4
			1174 w	1152 w		
				1174 w		

vs = very strong.
mw = medium weak.
w = weak.
wbr = broad weak.

Some of the hydration and degradation products, ettringite and thaumasite, formed on/in concrete due to the reaction with soluble sulphate ions can also be studied by means of Raman spectrometry and results have been reported by various authors [1,4,11–13]. Bensted [1] characterized ettringite in 1976 by means of VIS Raman spectrometry and assigned the highest intensity shift to the symmetric sulphate vibration at 1015 cm^{-1} and the antisymmetrical stretching at 1140 cm^{-1}. In more recent work ettringite is normally reported together with thaumasite and it was reported by Brough and Atkinson [11] that ettringite can be distinguished from thaumasite due to its wider peak observed at the symmetric stretching of the sulphate ion at around 1010 cm^{-1}, apart from the fact that it lacks the distinctive ν_1 Si(VI) shift. Jallad et al. [12] assigned the ν_1 sulphate vibrations to the shift observed at 988 cm^{-1} with lower intensity shifts at 449, 548, 617 and 1083 cm^{-1}. They used NIR excitation of 785 nm. In the paper written by Sahu et al. [13] similar conclusions were drawn. Raman shifts obtained by means of a 532 nm laser as excitation source were detected at 990 and 1086 cm^{-1}. Raman studies on thaumasite were reported by several authors [4,11–13] and a review article on its background and nature of deterioration in cement, mortars and concrete has been published by Bensted [14] in 1999. All the Raman shifts have been assigned by Bensted and are as follows: ν_1 sulphate vibration at 993 and ν_2 sulphate vibration at 459 cm^{-1}. The observed shift at 1077 cm^{-1} is assigned to the ν_1 carbonate vibration and the other shifts at 663, 431, 258 and 210 cm^{-1} were tentatively assigned to the ν_1, ν_2, ν_4 and ν_5 vibrations of SiO_6 respectively. Bensted suggested that the use of Raman spectroscopy with respect to thaumasite sulphate attack should and could be more extensively exploited. Brough and Atkinson [11] subsequently published a micro-Raman study, using various VIS excitation sources to investigate thaumasite in its pure mineral form, in concrete samples and synthetically prepared samples. Assignments of Raman shifts were the same as reported by Bensted and shifts were observed at nearly the same wavenumbers. Jallad et al. [12] and Sahu et al. [13] followed by presenting results obtained from Raman imaging, whereby the thaumasite could be identified and mapped to obtain a two dimensional spatial distribution. In the case of Jallad et al., NIR excitation was used and, in the case of Sahu et al., a VIS excitation source. Both these research teams characterised thaumasite in the same way as Bensted and Brough and Atkinson. Raman shifts obtained differed from each other with less than 3 cm^{-1}. The chemical imaging proved to be superior to XRD and SEM analysis in distinguishing between gypsum, ettringite and thaumasite. The potential for mapping the spatial distribution of these three compounds on the surface of sulphate attacked concrete samples could play a major role in assessing the type and extent of such an attack.

3. Characterisation of cement phases

A summary of Raman shifts as presented in various papers is given in Table 2. The Raman shifts for the pure mineral phases and those in the clinkers investigated with visible excitation sources gave similar results. Triclinic alite (C_3S) and monoclinic alite in OPC have been assigned a ν_1 SiO_4 vibration ranging from 840 to 848 cm^{-1}, with satellite shifts ranging from 813 to 890 cm^{-1}. A bending vibration has been assigned to the shift at 580 cm^{-1}. Belite (βC_2S) has been assigned a ν_1 SiO_4 vibration ranging from 860 to 864 cm^{-1}. C_3A has been assigned a ν_1 AlO_4 vibration ranging from 756 to 760 cm^{-1}. A bending vibration has been assigned to the shift at 508 cm^{-1}. The Raman shifts for the pure mineral phases and those in the clinkers investigated with a NIR excitation source (1064 nm) also gave results that correlated well with each other, as indicated in Table 2, but differed significantly from the shifts observed with VIS excitation with respect to the silicate phases. A fair amount of correlation is however observed between the Raman shifts obtained for the aluminate phases with both VIS and NIR excitation.

The first study of pure cement mineral phases, as well as white and ordinary Portland cement (OPC) has been reported by Bensted [1]. He found strong Raman inelastic scattering for: tricalcium silicate (C_3S) at 848 cm^{-1}; alpha dicalcium silicate α'-C_2S) at 828 and 864 cm^{-1}; beta dicalcium silicate (β-C_2S) at 864 cm^{-1} and assigned it to the ν_1 SiO_4 vibraton. A medium Raman scatter was observed for the tricalcium aluminate (C_3A) phase at 740 and 756 cm^{-1} and assigned to the ν_1 AlO_4 vibration. Bensted used an Ar^+ laser with a wavelength of 488 nm and a He–Ne laser with a wavelength of 632.8 nm as excitation sources.

Table 2
Summary of the observed Raman shifts for mineral phases, pure and in cement, using different excitation sources

Ref.	Conditions	Raman shift (cm^{-1})							
		C_3S triclinic	C_3S alite (WC)	C_3S alite (OPC)	α-C_2S	β-C_2S	C_2S belite (WC)	C_2S belite (OPC)	C_3A
1	514+632 nm	848 s			828 s	864 s			740 m
		852 w			864 s	852 sh			756 m
					892 s				
2	1064 nm	570 s		650 s		805 s			760 w
		940 wbr		1000 wbr		730 m			510 w
				1400 wbr					
	514+632.8 nm	840							
		890							
5	514.5 nm	845 s	845 s	845 s		860 s	860 s	848 s	
		855 s	832 m	832 s		848 s	848 s	860 s	761 ms
		813 m		750 mbr		900 m	900 w	740 mbr	508 m
		885 m				979 m	980 m		
						535 m	540 w		
						556 w	558 w		
						512 w	522 w		
6	1064 nm	541 s		666 s		799 s			504
		798 w		1017 w		722 w			753
		925 wbr		1431 w		1016 sbr			1083
		1340 wbr				1390 wbr			1525
7	1064 nm	574 sbr				1023 sbr			1050 mbr
		626 sh				1105 sh			
		1007 w				1376 wbr			
		1393 wbr							
	514 nm	842 s				856 s			
						972 m			
						1084 w			
8	514.5 nm	840 s							
		809 ms							
		880 ms							
		850 s							
		518 w							
		542 w							

vs = very strong.
s = strong.
ms = medium strong.
m = medium.
mw = medium weak.
w = weak.
br = broad.
sh = shoulder.

Similar work was conducted by Conjeaud and Boyer [5] in the 1980s. Pure cement mineral phases and industrial clinkers (white cement and OPC) were analysed by means of a micro-Raman spectrometer equipped with an Ar^+ laser of wavelength 514 nm. They distinguished between triclinic C_3S and the monoclinic alite present in white cement. The Raman spectrum for the pure phase indicates the highest intensity line at 845 cm^{-1} which was indicated as characteristic for C_3S, and satellite lines at 813, 885, 895, 903, and 917 cm^{-1}. Broadening of lines observed with the alite is ascribed to the increased disorder introduced by foreign ions present in the white cement. The highest intensity was at 845 cm^{-1} and a new line at 832 cm^{-1} could not be assigned. The alite in OPC had a similar fingerprint, but the intensity of the line at 832 cm^{-1} was higher than in the white cement and furthermore a broad shift around 750 cm^{-1} was assigned to the presence of ferric ions. Beta dicalcium silicate (β-C_2S) showed the same main lines for the ν_1 SiO_4 symmetric vibration at 848 and 860 cm^{-1} with the highest intensity at 860 cm^{-1}. The belite in the white cement had a similar fingerprint, but the belite in OPC again showed broadening of the scattering and also had a broad Raman shift at 749 cm^{-1} indicating the presence of ferric ions.

Another study was performed by Bonen et al. in 1994 [6] whereby analysis was done by means of FT-Raman using the 1064 nm laser as excitation source. They analysed synthetic cement mineral phases and commercial clinkers. Both the pure mineral phases and the commercial clinkers differed in the Raman spectrum fingerprint from results obtained by Bensted [1] and Conjeaud [5]. Neither of these two researchers has however used FT-Raman with a 1064 nm excitation source. There is on the other hand some correlation with the results obtained by Newman et al. [2], who compared results obtained by near infrared (NIR) and visible excitation. The studies of Bonen et al. in 1994 [6] and Dyer and Hendra (1993) [7] are much less comparable, as can be seen from Table 2. Bonen et al. distinguished between tri- and monoclinic structures of C_3S, as well as between the C_3S in clinkers produced under oxidizing and reducing conditions. Similarly they could distinguish between synthetically prepared β-C_2S and those produced under oxidizing and reducing conditions. A summary of the main Raman shifts as presented by Bonen et al. is presented in Table 3.

Dyer and Hendra [7] analysed pure phases with NIR FT-Raman and with dispersive Raman using 514.5 nm excitation. The intensity and disparity of the 1064 nm scattering observed by them, made them conclude that these shifts may be considered as non-vibrational in origin and probably due to fluorescence. They concluded that NIR excitation is not suitable for routine analysis of cements and concretes and that no proof could be found that the presence of rare earth elements (REE) is responsible for such high fluorescence phenomena. In 1995 a study of the hydration behaviour of C_3S was published [8], in which the triclinic mineral phase was also characterised before the hydration was studied. The respective Raman shifts are depicted in Table 2 and are in good agreement with results from Bensted [1], Newman [2], Conjeaud and Boyer [5] and Dyer and Hendra [7] obtained with VIS excitation. Bensted also reported the results for the analyses of γ-C_2S [4] and indicated that the main silicate stretching vibration is seen at 819 cm^{-1}, with a medium intensity shift at 840 cm^{-1}.

Table 3
Summary of Raman shifts obtained by Bonen et al. [6] with 1064 nm FT-Raman

Phase	Raman shift (cm^{-1})				
	Strong	Medium strong	Medium	Weak	Unclassified
C_3S					
Triclinic	541		798	925; 1340 br	
Monoclinic	593			935; 1361 br	
Oxidizing	663 (657–682)			1040; 1464 br	
Reducing	669 (658–682)			1002; 1439 br	
C_2S					
β-C_2S	799; 1016	1116 sh		722; 1389 br	
Oxidizing	1030 (1019–1040)	1112 sh	1459 (1442–1470)		
Reducing	980 (951–1020)	1125 sh	1462 br		
C_3A					
Cubic					504; 753; 1083; 1525
Orthorhombic					493; 521; 763; 1078
C_4AF					581; 1064

vs = very strong.
s = strong.
ms = medium strong.
m = medium.
mw = medium weak.
w = weak.
br = broad.
sh = shoulder.

The most recent research article by Newman et al. [2] reports on the analyses of pure mineral cement phases and 3 different OPCs with 1064, 632.8 and 514.5 nm excitation. They concluded that the observed scattering of the C_3S and C_2S phases, both in the pure and clinker phases, was purely due to a fluorescence phenomenon, since no anti-Stokes scattering could be observed when using the 1064 nm excitation laser. According to Newman et al. the spectrum obtained for the C_3A phase with shifts at 760 and 510 cm^{-1} respectively are true Raman shifts, since it was also observed by Conjeaud and Boyer [5]. Raman spectra of C_3S recorded by using two different visible lasers are also shown and indicated shifts that agree reasonably well with those obtained by Bensted [1] and Conjeaud and Boyer [5]. The authors therefore concluded that since these Raman shifts seem to be independent of the wavelength of the excitation source, it must be true. Newman et al. [2] went one step further and analysed various purities of monocalcium silicate with 1064 nm excitation. It was found that the 99% pure monocalcium silicate, showed very little fluorescence. True Raman shifts were identified by performing anti-Stokes analysis. The less pure monocalcium silicate did have some broad fluorescence shift in the region of 980 cm^{-1}, but the true Raman shifts were still observed clearly, although superimposed on a fluorescent background. The dicalcium silicate of the same purity (99%), analysed under the same conditions, did however, once again give the structured fluorescence observed for all the pure mineral cement phases. They eventually concluded that a possible explanation could be the difference in status of the compounds with respect to the arrangement of the silicate tetrahedra.

Lack of reporting exact experimental conditions in all the papers cited here, makes the interpretation of small variations difficult. The sample preparation is also not always specified, neither is the instrument's configuration. In the cases of Conjeaud and Boyer [5] and Bonen et al. [6] it was specified that the preparation of polished sections was required to analyse the cement samples. It does seem as though Newman et al. [2] used the samples "as is", although results for the cement clinker analysed are not presented in the paper. In the review by Bensted [4] the final conclusions included that the use of Raman spectroscopy is useful if it is applied to white Portland cements and its constituents and that developments with regard to microprobe and FT-Raman led to greater resolution and extended applications. He specifically reported that the poor Raman scattering from the grey coloured OPC clinkers severely limit the use of Raman spectroscopy in these samples. The advantage of improved spectral resolution due to (among other factors) a smaller spot size of the micro-Raman configuration, as well as the availability of various wavelength lasers as excitation sources, has certainly not been fully exploited in its application to grey cements. The further advantage of Raman chemical imaging and point-to-point mapping, to facilitate the identification and distribution profile of the various cement phases in especially grey cements, has not been investigated.

4. Cement hydration

The Raman activity during the hydration of pure cement phases, white cement and OPC has been reported as early as 1976 [1]. In principal the hydration of the alite and belite phases take place due to monomeric silicates uniting to form a nearly amorphous calcium hydrosilicate (C–S–H) gel, together with crystalline calcium hydroxide (CH). The C–S–H has variable compositions due to the calcium:silicon ratio and the hydrometry conditions. Since the C–S–H is amorphous in nature and therefore poor in crystallinity, its inelastic scattering is inherently low in intensity. Despite this shortcoming, Raman spectroscopy has been used successfully to investigate the hydration behaviour of pure phases and cement, both qualitatively and quantitatively.

The first work reported was done by Bensted [1], whereby the degree of hydration of white Portland cement has been followed by recording the decrease in intensity of the main Raman shifts of alite and belite, with the use of 488 nm excitation. In addition the evolution of gypsum hydration can be used to follow the hydration process. The initial stretching vibration of the sulphate anion shifts slightly (from 1010 to 1015 cm^{-1}) due to the initial formation of ettringite and then a shift to 994 cm^{-1} is observed due to the formation of the monosulphate. The formation of calcium hydroxide could also be monitored due to the ν OH inelastic scattering, observed at 355 cm^{-1}. Bensted reported that due to poor crystallinity C–S–H did not show any detectable bands, but by quantification of the diminution of the alite and belite shifts, the hydration could be studied.

Conjeaud and Boyer [5] investigated synthesized C–S–H, hydrated C_3S ($w/C_3S=10$) and hydrated OPC (w/c 0.5), using 514.5 nm excitation. The samples had to be prepared as thin polished sections, in order to obtain spectra. They observed some Raman activity at 670 cm^{-1} for the synthesized C–S–H, but could not get any Raman shifts for the C_3S hydration and reported a shift at 640 cm^{-1} for the OPC. This was assigned to Si–O–Si symmetric stretching, with the difference in shift assigned to the presence of Al and Fe.

Tarrida et al. [8] in 1995 reported the results of a quantitative and qualitative in situ study of the hydration of pure C_3S, by means of 514.5 nm excitation. They also identified the Si–O–Si symmetric stretch at 662 cm^{-1} for synthesized C–S–H and at 640 cm^{-1} in cement pastes. A decrease in intensity of the C_3S shift has been correlated to an internal standard quantity of TiO_2. The result of this study indicated a 1-day hydration of 46%, which correlated well with previous studies by Maggion, but not so well with results obtained by Bensted and Justnes, as reported by Tarrida et al. [8].

In the review paper of Bensted [4] he reports on a number of investigations concerning cement hydration, in which he was involved. In an investigation done by him in 1976 it was found that the otherwise thought, non-hydraulic γ-C_2S, was in actual fact hydraulic and reacted to form C–S–H with hydration although the reaction rate is much slower than that for α-C_2S, α'-C_2S and β-C_2S.

Kirkpatrick et al. [15] performed a Raman study of C–S–H, tobermorite and jennite in 1997 in order to establish the structural relationship between single phase C–S–H of various C/S and tobermorite and/or jennite. Synthesized C–S–H samples with C/S ranging from 0.88 to 1.45 and C–S–H with portlandite (C/S greater than 1.54), as well as 11 Å and 14 Å tobermorite and jennite were investigated. Raman scattering was initialised by means of VIS laser excitation of 488 nm using a 180° backscattering geometry. The symmetrical Si–O stretching for C–S–H was found to be at 1005 cm^{-1} irrespective of the C/S ratio. The main Si–O–Si bending mode for all the C–S–H samples was found to be at 664–669 cm^{-1}, while the internal deformations of the SiO_4 tetrahedra are at 450 cm^{-1}. The shift observed at 325 cm^{-1} is assigned to OH translational modes. Kirkpatrick et al. concluded that all the C–S–H samples show a structure that is similar to that of tobermorite, although some jennite-like structures were observed in localized domains.

Three different cements were analysed by Newman et al. [2], using NIR FT-Raman. Although the shifts observed were unambiguously assigned to structural fluorescence, the authors were of the opinion that the progressive decrease in the intensity of these bands can be used to describe the hydration process. The most significant changes were observed between 3 and 48 h and the authors concluded that it is possible that the reduction of fluorescence may be ascribed to the polymerization process, which subsequently reduces the discrete tetrahedral silicates. This would then support their indication that the fluorescence observed is due to the C_2S and C_3S containing discreet tetrahedral silicates that are not linked as in the case of CS where such fluorescence was not observed.

5. Carbonation studies

As explained by Bensted [16], carbonates are frequently encountered in cement chemistry and normally exist in the form of calcite ($CaCO_3$). The symmetrical stretching, ν_1, of the carbonate ion, as well as the antisymmetrical, ν_3, and angle bending, ν_4, are all Raman active. The very strong inelastic scattering vibration ν_1 CO_3 is used to assess carbonation in cement minerals [4]. Bensted [17] in 1977 showed the value of following the growth or diminution of the ν_1 CO_3 shift, which he assigned at 1090 cm^{-1} using VIS excitation, in studying the carbonation effects on ettringite, C–S–H, monosulphate and white Portland cement. Other researchers [2,6] assigned a wavenumber of 1087 cm^{-1} to this stretching vibration, which also correlates well with what is currently available in the open literature for calcite. The most recent paper on this topic was written by Martinez-Ramirez et al. [18]. They reported on a study of the characterisation of the different polymorphs of calcium sulphate dihydrate in a depth profile of a cement mortar exposed to carbonation, by using micro-Raman spectrometry. Identification of calcite, aragonite and vaterite was mainly done with the use of FT-Raman using 1064 nm excitation and the micro level analysis required for the depth profile was done with the use of a dispersive micro-Raman instrument using 785 nm excitation. A summary of the observed Raman shifts, together with their respective vibrational assignment is reported in Table 4. The authors could not succeed in quantifying the relative amounts of the two polymorphs, calcite and aragonite respectively, found in the mortar.

6. Conclusions

The application of Raman spectroscopy to investigate and characterise cementitious materials and systems offers several advantages. Easy in situ recording of the materials and their subsequent reactions without the need to remove moisture from the sample or elaborate sample preparation procedures, are possible without compromising results. Small sample masses and structural identification capabilities at a much lower detection limit than is possible with the XRD technique can be achieved, especially with the use of micro-Raman configurations. This configuration also allows the ability to monitor changes in chemical composition and morphology on a microscale. The possibility to distinguish between the behaviour of various crystallographic structures of the same phase or mineral can be studied. Qualitative and semi-quantitative measurements of amounts of various components of the system are relatively easy and investigations into this application on a routine basis deserve attention.

Hydration reaction rates and/or degradation reactions can be estimated. The technique allows the ability to recognise oxidizing and reducing production conditions with minimal sample preparation and without resorting to more laborious optical microscopic techniques. The resulting corrective actions in the case of reducing production conditions can potentially save costs and optimise raw material consumption. The ability to monitor carbonation in hydrated cement provides a mechanism to assess the risk of corrosion of steel reinforcement that can be used in conjunction with electrochemical techniques.

The characterisation of the various cement mineral phases in grey cement received very little attention, probably due to the large fluorescent background observed when VIS and NIR excitation are used. This aspect could certainly be further

Table 4
Summary of the observed Raman shifts of the different polymorphs of gypsum, together with their respective vibrational assignment, as reported by Martinez-Ramirez et al. [18]

Reference	Conditions	Raman shift (cm^{-1})			
		Calcite	Aragonite	Vaterite	Assignment
[17]	1064 nm 785 nm		852–854 vw	Unassigned Very weak	ν_2 CO_3
		712 w	700+704 w doublet	740+750 w doublet	ν_4 CO_3
		1085 vs	1085 vs	1074 vs+1090 vs doublet	ν_1 CO_3
		1450 w	Unassigned very weak	Unassigned very weak	ν_3 CO_3
		280 w	205 w	300	Lattice vibration

vs = very strong.
s = strong.
ms = medium strong.
m = medium.
mw = medium weak.
w = weak.
vw = very weak.
br = broad.
sh = shoulder.

exploited, especially with the aid of mapping features to illustrate the distribution profile of the various phases. Very little work could be found in the literature on Raman investigations on secondary cementitious materials (SCMs), indicating that this might be an area requiring some attention in future.

Acknowledgements

SSPV gratefully acknowledges financial support from the University of Antwerp and the FWO (Fonds voor Wetenschappelijk Onderzoek, Vlaanderen) for financial assistance.

References

[1] J. Bensted, Cem. Concr. Res. 59 (1976) 140.
[2] S.P. Newman, S.J. Clifford, P.V. Coveney, V. Gupta, J.D. Blanchard, F. Serafin, D. Ben-Amotz, S. Diamond. Anomalous fluorescence in near-infrared Raman spectroscopy of cementitious materials. Cem. Con. Res. 35 (8) 1620 (in press).
[3] S.N. Ghosh, S.K. Handoo, Cem. Concr. Res. 10 (1980) 771.
[4] J. Bensted, Colloquium on Techniques for Characterisation of Cement Hydration—New and Old Techniques, Society of Chemical Industry Constructions Materials Group, London, 1999.
[5] M. Conjeaud, H. Boyer, Cem. Concr. Res. 10 (1980) 61.
[6] D. Bonen, T.J. Johnson, S.L. Sarkar, Cem. Concr. Res. 24 (1994) 959.
[7] C.D. Dyer, P.J. Hendra, Spectrochim. Acta 49 (5/6) (1993) 715.
[8] M. Tarrida, M. Madon, B. LeRolland, P. Colombet, Adv. Cem. Based Mater. 2 (1995) 15.
[9] J. Bensted, ZKG 9 (1976) 416.
[10] P.S.R. Prasad, A. Pradhan, T.N. Gowd, Curr. Sci. 80 (9) (2001) 1203.
[11] A.R. Brough, A. Atkinson, Cem. Concr. Res. 31 (2001) 421.
[12] K.N. Jallad, M. Santhanam, M.D. Cohen, D. Ben-Amotz, Cem. Concr. Res. 31 (2001) 953.
[13] S. Sahu, D.L. Exline, M.P. Nelson, Cem. Concr. Compos. 24 (2002) 347.
[14] J. Bensted, Cem. Concr. Compos. 21 (1999) 117.
[15] R.J. Kirkpatrick, J.L. Yarger, P.F. McMillan, P. Yu, X. Cong, Adv. Cem. Based Mater. 5 (1997) 93.
[16] J. Bensted, Cem. Technol. (1975 (Sept/Oct)) 161.
[17] J. Bensted, Cem. Concr. Res. 7 (1977) 161.
[18] S. Martinez-Ramirez, S. Sanchez-Cortes, J.V. Garcia-Ramos, C. Domingo, C. Fortes, M.T. Blanco-Varela, Cem. Concr. Res. 33 (2003) 2062.