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Absorption and reflection infra-red spectra of major cement minerals, clinkers and cements

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The infra-red spectra of the major cement minerals, synthetic mixes of the four important clinker phases and commercial clinkers and cements have been studied both by the absorption technique as well as by the attenuated total reflectance technique of powder samples. The possibility of general application of infra-red spectrometry in the quality control of clinkers and cements has been indicated especially with reference to the relative proportion of the tricalcium and dicalcium silicate phases. In this context the potentiality of the attenuated total reflectance technique in cement characterization has been especially emphasized.

1. Introduction

In the field of cement chemistry the infra-red spectrometry is a comparatively new tool of material characterization, the scope of application of which has not yet been firmly established. This is mainly because of the fact that the infra-red bands of cement minerals and cements are generally broad and intense, and show an overlap in their frequency ranges. The restricted application of infra-red spectrometry has also been due to the limitation of the conventional KBr disc method of sample preparation, in which the highly hygroscopic nature of both KBr and cement materials may lead to certain inaccuracies of results.

Recently the problem of sample preparation has been partially overcome by the introduction of infra-red reflection spectra studies of powder samples. Although this technique has not yet been practised for cement characterization, it has, nevertheless, shown encouraging results in allied fields. Therefore, it is worthwhile to try this potential technique for cement characterization, if not immediately for routine analysis, at least for evaluating the absorption spectra by direct comparison.

In view of this and also in view of the fact that until now the major bulk of infra-red studies related mainly to the hydrated cement phases [1-3], a systematic investigation of the anhydrous clinker phases and clinkers by infra-red spectrometry deserves special attention. In this connection mention may be made of some recent studies where infra-red spectrometry has been attempted as an analytical tool [4, 5]. Of all the clinker minerals C_3A has received the widest attention of the investigators [6-8]. However, in spite of these investigations, there is still a wide divergence of views, which makes the present study all the more justified.

The present investigation has been planned to study the characteristic variation of infra-red spectra of the two structurally differentiable groups of clinker phases – the calcium silicates, and aluminates/alumino-ferrites, to find out the composite spectra of the synthetic mixes of the above two groups and to compare the infra-red spectra of commercial cements and clinker with those of synthetic mixes and individual phases. The usefulness and adaptability of infra-red reflection powder spectra for routine analysis purposes has also been considered. The available frequency values of Si–O and Al–O motifs are also taken into consideration and a theoretical approach for better understanding of solid state infra-red spectra using factor group analysis has also been indicated. The ultimate scope of application of our preliminary findings has been illustrated on the basis of parallel studies of samples by X-ray diffractometry and infra-red spectrometry.

2. Experimental

2.1. Synthesis

The pure clinker phases (tricalcium silicate, dicalcium silicate, tricalcium aluminate and calcium aluminoferrite) were synthesized in 20 g quantities from analytically pure $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3, mixed in stoichiometric proportions, pelleted, and repeatedly fired at appropriate temperatures in electric resistance furnaces with intermediate grinding before refiring. β–C_2S* was stabilized from synthesized γ–C_2S by controlled heating of minus 325-mesh γ–C_2S sample and air quenching without any introduction of external stabilizers. The aluminoferrite phase corresponded to the composition C_6AF_2 in the solid solution series C_2F–C_6A_2F. This was done in view of the fact that in most of the Indian clinkers the composition of the aluminoferrite phase falls in the neighbourhood of C_6AF_2. The purity of the synthesized phases was checked by X-ray diffractometry using Cu$K\alpha$ radiation in a Philips Diffractometer fitted with a GM counter. The same set-up was used for taking X-ray diffraction patterns of synthetic and commercial clinkers and cements.

2.2. Infra-red spectrophotometry

The infra-red spectra of these compounds, mixes, and commercial clinkers and cements were taken in the range of 4000 to 200 cm^{-1} using Perkin-Elmer Model 621 spectrophotometer. The instrument was calibrated using polystyrene and indene. The estimated accuracy is about $\pm$ 2 cm^{-1}. For absorption spectra analytically pure potassium bromide was used to make pellets at a total pressure of 700 kg cm^{-2}. Liquid paraffin was used in the case of mull-spectra on potassium bromide discs and polyethylene (2 ml thick) plates.

The reflection spectra of powdered samples (325 mesh) were taken using Perkin-Elmer attenuated total reflectance attachment and KRS-5 crystal. The angle of incidence was approximately set at 45°.

3. Absorption spectra

The fundamental modes which can give rise to infra-red bands for these compounds are certainly of the types such as stretching, bending, torsion and lattice modes, of which stretching and bending modes are of concern to our present study. They may be simple or more likely coupled vibrations and several parameters such as structure, bond strength, point symmetry and crystal symmetry, etc. play an important role in the number, position and structure of the infra-red bands.

3.1. Calcium silicate group

Of all the inorganic minerals the silicate group has been most widely and intensively studied by infra-red spectrometry. Launer [9] has given a table summarizing the strong absorption bonds of silicates with different Si–O motifs (Fig. 1). The figure indicates that when Si:O ratio increases from 0.25 in the isolated tetrahedra in the orthosilicates to 0.50 in the three-dimensional network of quartz, the absorption band shifts to shorter wavelengths and the frequency range shows a tendency to become narrower.

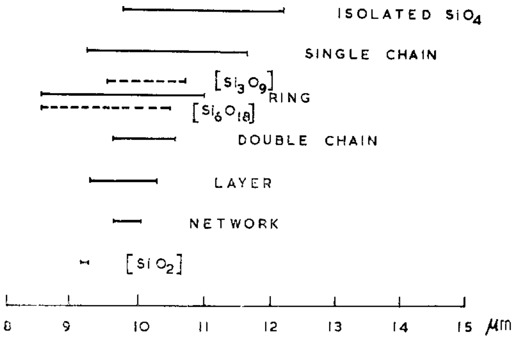

Figure 1 Relation between the silicate structure and frequency range in absorption spectra.

The silicate group of clinker phases consists mainly of C_3S, β–C_2S and sometimes γ–C_2S and rarely α'–C_2S. All these phases belong to the orthosilicate group, C_3S being represented by the structural formula Ca_3O $[SiO_4]$. Therefore, infra-red spectra of these silicates are characterized by the stretching and bending modes of Ca–O and Si–O motifs occurring in different frequency ranges. With this background information C_3S, β–C_2S and γ–C_2S will be considered individually. The absorption bands are listed in Table I.

3.1.1. γ-C_2S

This phase is reported to be isostructural with monticellite [10] having isolated SiO_4 tetrahedra and regular six-fold co-ordination of calcium with oxygen. In the infra-red absorption spectra of this phase, four distinct spectral ranges can be delineated: 1000 to 800, 800 to 600, 600 to 400 and less than 400 cm^{-1}. The most intense band a 850 cm^{-1} and the second most intense band at

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*$CaO = C$; $Al_2O_3 = A$; $Fe_2O_3 = F$; $SiO_2 = S$.

TABLE I Absorption infra-red bands (cm^{-1}) in cement minerals/cements

C_3S	β–C_2S*	γ–C_2S	C_3A	C_6AF_2	NBS/SRM	Synthetics		CC1	CC2
						1*	2*		
995	995	950 m	894 s	693 s, br	1115 s, br	1050 sh	992	1107 w, sh	1110 w, sh
903 s, br	972	850 s	865 s	605 s	925 s, br	992 w	940	1003 w, sh	990 w, sh
846 sharp	940	820 sh	845 sh	554 s, br	750 s, br	930 m	915	920 s, br	970 vw, sh
798 sh	845 s	690 w	820 s		665 m	915 m	850 s	870 sh	920 s
692 w	815 sh	668 w	787 w		600 sh	850 s	815	842 sh, m	875 s
520 s	690 w	565 m	765 w		524 s, br	815 sh	713 w, sh	815 sh	855 s
	668 w	520 s	741 s		450 m, br	715	560 s	725 w	845 sh
	565 s, sh	495 s	707 s			560 s	518 s, br	620 w	712 w
	520 s	440 m	610 w, br			520 s	498 sh	570 w, sh	535 w, sh
	500 s	360 s	580 m			497 s	455 w	520 s	522 s
	440 m		540 sh			452 w	441 m	450 w, br	460 w, br
	360 m		522 m			440 m			
			510						
			465 m						
			411 m						
			385 w						

*The strong band envelope in the region 1000 to 800 cm^{-1} is not quite resolvable.
br = broad; sh = shoulder; s = strong; m = medium; w = weak; vw = very weak

950 cm^{-1} and the shoulder at 820 cm^{-1} characterize the stretching modes of SiO_4 group. Under ideal conditions no absorption bands are expected in γ–C_2S in the range 800 to 600 cm^{-1} [11]. However, the weak bands that appear in our spectra in the range 700 to 650 cm^{-1} (Table I; the corresponding bands in Fig. 3 are not visible due to the difficulties of reproduction and amount reduction) may possibly indicate some deformation in the structure induced probably by a marginal transition of isolated tetrahedra to (Si_2O_7) anionic complex, similar to that in rankinite. In the range 600 to 400 cm^{-1}, the moderately intense bands at 565, 520 and 495 cm^{-1} may be ascribed to the deformation modes of isolated tetrahedra. Although the absorption bands below 450 cm^{-1} are generally ascribed to cationic complexes and low energy modes, in the case of γ–C_2S the absorption band of 440 cm^{-1} is ascribed to the deformation modes of SiO_4 tetrahedra [12]. The band at 360 cm^{-1} may be attributed to the cationic modes.

3.1.2. β-C_2S

This is a monoclinic modification of γ–C_2S with tetramolecular cell [10]. In this phase the oxygen co-ordination of calcium is irregular, being six-fold for 4 Ca ions and eight-fold for the remaining Ca ions.

The broad pattern of spectra is very similar to that of γ–C_2S with the variation of appreciable broadening of the absorption band in the spectral range 1000 to 800 cm^{-1} and more conspicuous splitting of the spectral bands in the range below 400 cm^{-1}.

An interesting observation of the KBr spectra of β–C_2S is that a strong shoulder at 565 cm^{-1} is absent in the corresponding Nujol spectra (Fig. 2). γ–C_2S has this shoulder at 565 cm^{-1} both in Nujol and KBr spectra. The reason for this phenomenon may be ascribed to the known conversion of β–C_2S to γ–C_2S under pressure or impact as otherwise reported [13].

3.1.3. C_3S

This compound is reported to be pseudohexagonal with elementary cell of 9 molecules. Although the co-ordination number of calcium is 6, it is irregular in disposition with oxygen ions concentrated on one side of each Ca ion leaving holes to accommodate another Ca ion thereby causing higher lattice energy.

The broad pattern of infra-red absorption spectra is comparable to that of the dicalcium silicate phases. However, in the range 1000 to 800 cm^{-1} there is a distinct shift of the most intense band from 850 to 845 cm^{-1} to 903 cm^{-1} and the medium-intensity band at 950 to 940 cm^{-1} to 995 cm^{-1} in C_3S but a sharp shoulder is retained at 846 cm^{-1}. The 565 cm^{-1} band in C_2S disappears in C_3S and a shoulder appears at 798 cm^{-1} (Fig. 3).

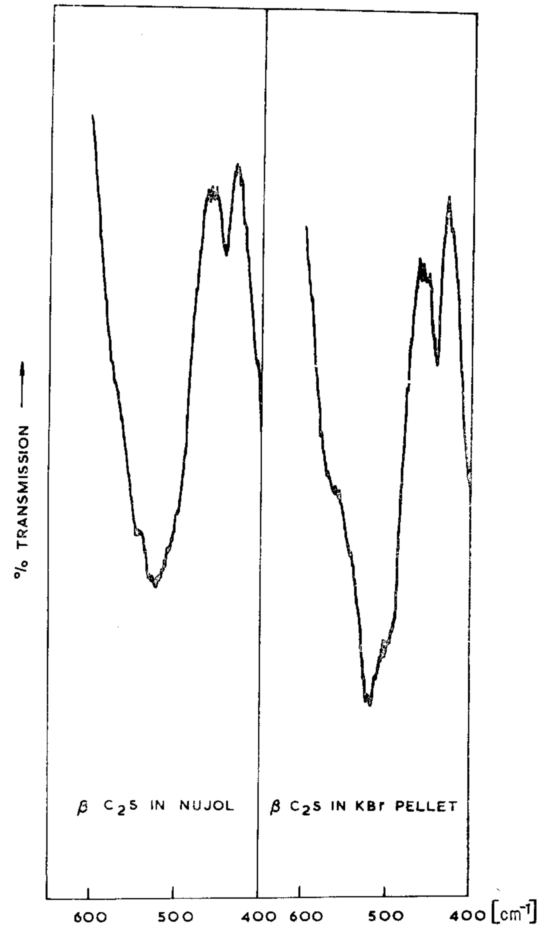

Figure 2 Shift in band position (in β-C_2S) due to sample preparation.

3.2. Calcium aluminate and aluminoferrite group

The calcium aluminate and aluminoferrite group of minerals are characterized by Al–O, Ca–O and Fe–O structural motifs with considerably different frequency ranges in their infra-red spectra. The stronger and more covalent Al–O bands are expected to give rise to higher frequency ranges than the other two cationic complexes. Any change of co-ordination characteristics of the Al ion from the four-fold to six-fold state will also result in lowering of bond energy and degree of covalency, which will, in turn, result in lowering of absorption frequency. There is a wide difference of opinion regarding the frequency ranges of AlO_4 and AlO_6 groups, which is evident from Table II. Nevertheless, some general deductions can be made regarding the aluminate and aluminoferrite group of clinker phases from a comparison of the spectra obtained by us with the data available from the literature.

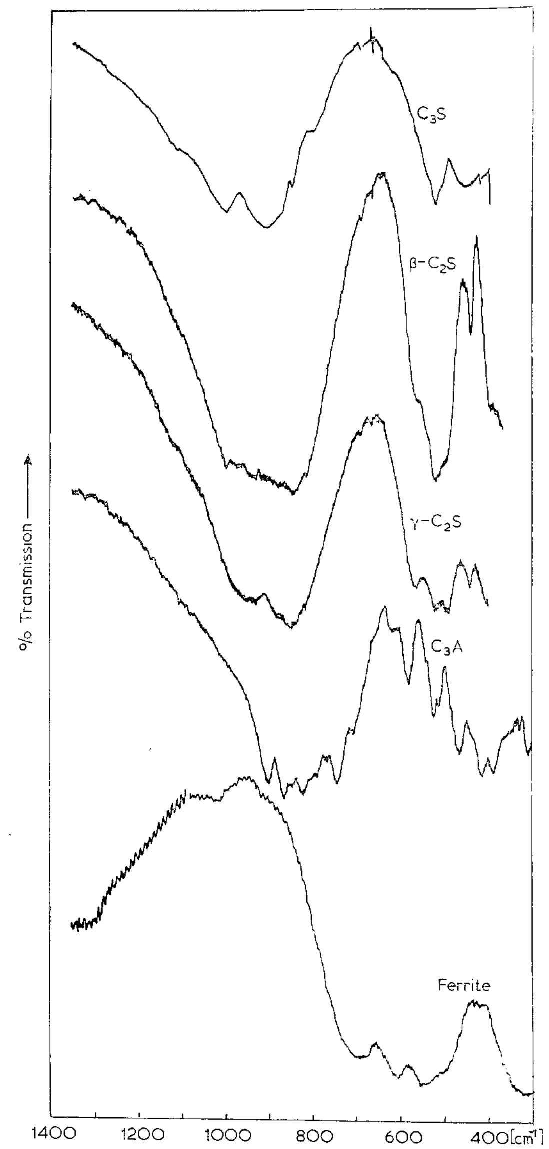

Figure 3 Absorption spectra of cement minerals.

3.2.1. C_3A

Tricalcium aluminate belongs to the cubic system with 24 molecules in the elementary cell. In spite of there being only one form of C_3A, its structure has not yet been acceptably defined, the doubtful features being the presence of an AlO_6 group and the exact co-ordination characteristics of the Ca ions.

The infra-red spectra of C_3A, obtained by us, are in good agreement with those that have been

TABLE II Characteristic infra-red frequencies (cm^{-1}) assigned in various aluminates [16-19]

Aluminates containing AlO_4 species	Aluminates containing AlO_6 species	Aluminates containing AlO_4 and AlO_6 species
870–700 in various aluminate	650–600 in α-alumina	820–560 in β-alumina
780–720 } in mono-aluminates 900–800 }	700–500 in spinel	
1165, 850, 730 in mullite	598, 548 in mullite	

published previously (Table III). In view of the non-availability of any clear structural picture of this phase, no assignments of bands to specific modes could be made. However, it may be tentatively generalized from the data given in Table II that if the frequency range above 700 cm^{-1} is ascribed to the modes of Si–O–Al motifs as indicated in [17] the frequency range 900 to 700 cm^{-1} may characterize the modes of condensed AlO_4 groups and the frequency range 700 to 500 cm^{-1} may be attributed to the vibrations of condensed octahedra, which also explains the overlapping range of 820 to 560 cm^{-1} observed in β-alumina containing both the AlO_4 and AlO_6 species. In accordance with this, the infra-red spectrum of C_3A shows the presence of condensed AlO_4 tetrahedra and indicates the existence of AlO_6 species. The bands below 500 cm^{-1} in C_3A spectra may be ascribed to the deformation modes as well as modes due to cationic groups.

TABLE III Infra-red absorption frequencies of tri-calcium aluminates in KBr pellet

Schroedor and Lyons [7]	Burdick and Day [6]	Present work
898 s	892 s	894 s
861 s	860 s	865 s
841 w	840 w	845 sh
818 S	815 m	820 s
803 w, sh	798 vw	787 w
787 w, sh	784 m	
760 w, sh	760 w	765 w
742 s	740 s	741 s
707 vw	704 m	707 s
645 m		
617 m		610 w, br
536 w, sh	540 m	580 m
520 ms	523 s	540 sh
509 ms	512 m	522 m
450–400 s	462 m	510 m
	416 s	465 m
	385 s	411 m
		385

However, it may be worthwhile to indicate here that, if the infra-red spectra of C_3A are compared with those of the calcium silicates, the moderately intense bands in the range 750 to700 cm^{-1} in C_3A spectra appear to be without any overlap in the spectral frequencies of the silicate phases and hence may be considered as distinctive.

3.2.2. C_6AF_2

The general structural delineation of the solid solution series C_2F–C_6A_2F has already been done [14]. The series is characterized by an orthorhombic cell belonging to the space group *Imma*–D_{2h}^{28} and containing 4 molecules of C_2F or equivalent solid solution. Al and Fe are in either four-fold or six-fold co-ordination and form two separate layers in the structure connected by common atoms of oxygen with calcium atoms in the interstices. This gives rise to ten-fold or six-fold co-ordination of calcium.

The infra-red spectrum of C_6AF_2 obtained by us, indicates absorption bands in the frequency range 700 to 500 cm^{-1} which hints at predominance of AlO_6 groups in the structure. The absence of bands in the range 750 to 700 cm^{-1} in C_6AF_2 spectra leaves the distinctiveness of this range in C_3A undiminished.

3.3. Synthetic and commercial clinkers and cements

In order to study the effectiveness of application of infra-red spectrometry for the analysis of clinkers and cements two synthetic mixes, two commercial clinkers, and one NBS/SRM cement were investigated (Table IV and Fig. 4).

If we now compare the phase compositions of the samples with the corresponding infra-red spectra, we will find that in the specimens synthetic 1 and 2 with C_3S in the range of 25 to 35 % and C_2S in the range of 45 to 55 %, the absorption bands in the frequency range 1000 to 800 cm^{-1} are broad with a peak at about 850 cm^{-1} whereas in NBS/SRM with C_3S content of 69.4 % and C_2S content of 9.1 %, the frequency range 1000 to 800 cm^{-1} shows a narrow band

TABLE IV Phase composition as determined by X-ray diffractometry

Phases	Synthetics		NBS/SRM	CC1	CC2
	1	2			
C_3S	35	25	69.4	50.7	46.1
β-C_2S	45	55	9.1	23.9	26.5
C_3A	10	15	10.8	11.5	12.4
Ferrite phase	10	5	6.3	11.4	7.8
MgO			1.2	2.3	7.1
Calcium sulphate			3.0		

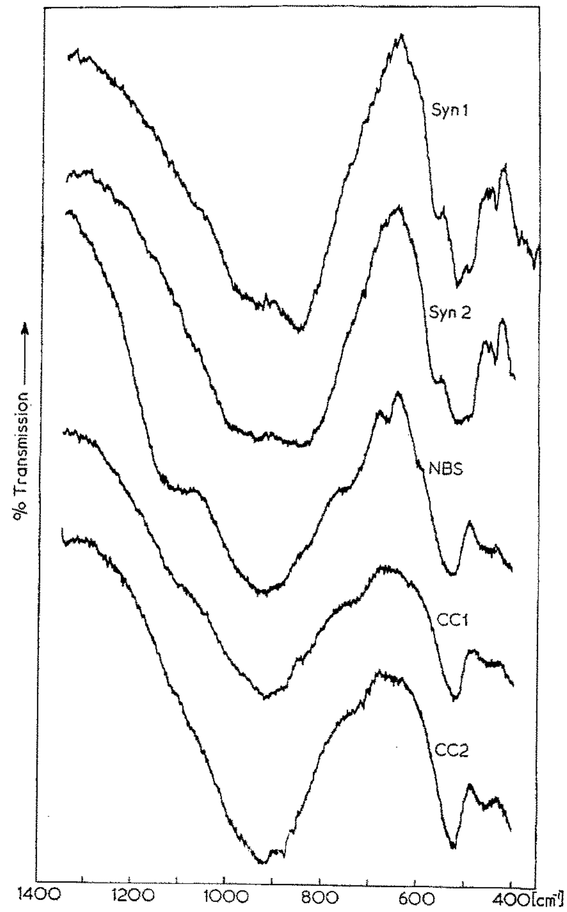

Figure 4 Absorption spectra of cement.

with a peak at 925 cm^{-1} approximately. Moreover, the absorption band at 560 cm^{-1} in synthetics 1 and 2 disappears in NBS/SRM. These characteristic frequency changes which are dependent on the relative proportions of C_3S and C_2S are also corroborated by infra-red spectra of CC1 and CC2. In the latter samples, the C_3S and C_2S contents are intermediate between synthetics 1 and 2 on one hand and NBS/SRM on the other and there is a tendency for intensification of two peaks in the 1000 to 800 cm^{-1} frequency range and the development of a 560 cm^{-1} band is either undetectable or feeble. The weak shoulders that develop in the range 750 to 700 cm^{-1} relate to the C_3A contents, while no specific assignments could be made to the aluminoferrite phase in the clinker spectra.

The comparatively high percentage of MgO in CC2 has apparently not introduced any recognizable change in the spectra over the range studied by us. This confirms that modes due to Mg–O vibration should be expected much lower than 400 cm^{-1} so far as the clinker phases are concerned.

A point worth mentioning here is that in some of the clinker runs the presence of carbonate was detected. In order to investigate the relative degree of succeptibility of different clinker phases to carbonation during atmospheric exposure, infra-red spectra were taken of six-month-old clinker phases. C_3S and the aluminoferrite phase indicated strongest succeptibility to carbonation with intense bands in the 1480 cm^{-1} range.

4. Reflection spectra

The attenuated total reflection spectra of powder samples have recently been reported to be of great significance due to the following reasons [15].

(1) A high absorbing medium can have a satisfactory reflection spectra with better details of band structure.

(2) The band positions in reflection spectra are nearly the same as in absorption spectra.

(3) Interaction between the matrix material and sample can be avoided.

The general pattern and band positions of the absorption and reflection spectra are in most cases equivalent and reproducible. (Tables I and V; Figs. 3 and 5). The characteristic absorption bands for C_3S around 1000, 900 and 800 cm^{-1}, for C_2S around 950, 850 and 565 cm^{-1}, for C_3A

TABLE V Reflection infra-red bands (cm^{-1}) in cement minerals/cements

C_3S	β-C_2S	C_3A	Ferrite	NBS/SRM cement
				1155 w
	995 m	892 m		1115 w
1025 w	980 w	855 s		1095 w
1000 w, br	947 sh	810 s		1015 w, br
905 s	928 sh	780 sh	812 sh	985 sh
885 s, br	875 br	738 s	705 s	938 sh
785 w	844 s	700 w	620 s, br	923 s, br*
680 w, br	680 w, br	680 w	520 m	910 sh
523 sh	625 w, br	618 w		898 sh
512 s	566 w, sh	608 w		845 m
	510 s	578 m		823 w
	440 w	570 sh		715 w, br
		520 m		605 w
		507 m		597 w
		455 s		532 sh
		400 s		525 sh
				519 s
				444 m

*The band in 923 cm^{-1} region is broad and splittings of this band occur at 938, 910 and 898 cm^{-1}.

in the range of 750 to 700 cm^{-1} and for the aluminoferrite in the range 700 to 550 cm^{-1} are distinctly discernible in their corresponding reflection spectra. The shift in the band positions is in the most cases only marginal. The resolution of the β-C_2S and C_3A reflection spectra is noteworthy. The reflection spectra of the cement sample (NBS/SRM) also needs special mention as it represents one of the best resolved spectra so far reported. The major absorption band position at 925 cm^{-1} in the stretching frequency region (Si–O) is clearly observed in the reflection spectra at 923 cm^{-1} of NBS cement sample. The bending region is also closely identical. The large number of bands in the reflection spectra of the cement sample is expected because of the composite nature of cement, which, however, is not evident from the absorption spectra. The slight shifting of other bands compared to the absorption spectra may primarily be accounted for by the interaction in the KBr pelleting. The fine structure of the stretching region clearly demonstrates the superiority of reflection spectra over absorption. However, it is difficult at present to assign all the bands to corresponding bands in the pure phases because of the possible effect of solid solution. A further study is warranted.

4.1. Factor group analysis

No firm quantitative assignment has yet been made of the cement mineral spectra mainly because of the complex nature of the compounds and absence of refined X-ray data on the structure of the compounds, especially of C_3A and aluminoferrite solid solution series. In view of this, the factor group analysis has also to be restricted to only C_3S and β-C_2S at the present moment. The space group for C_3S is C_{3V}^5 ($R3m$) with 9 molecules per unit cell [10]. It turns out that the total number of modes classified under $21A_1 + 6A_2 + 27E$, of which the total number of internal modes is $15A_1 + 2A_2 + 14E$. A_1 and E modes are infra-red active, so that the spectra should have at least 29 bands and actually 12 band have been observed in the range of our present study.

Similarly the space group for β-C_2S is $C_{2h}^5(P_{21/n})$ with 4 molecules per unit cell. The expected infra-red active internal modes turn out to be 12Au + 12Bu under the factor group C_{2h}. Actually 11 bands have been observed in the reflection spectra of our present study. Needless to say FGA calculations and quantitative assignments of cement mineral spectra will be possible at a future date with further acquisition of data and more detailed study in this direction.

5. Conclusion

1. Even without the specific assignment of spectral bands of cement minerals it is possible to use infra-red spectrometry as a tool in the broad quality control of cement and particularly in

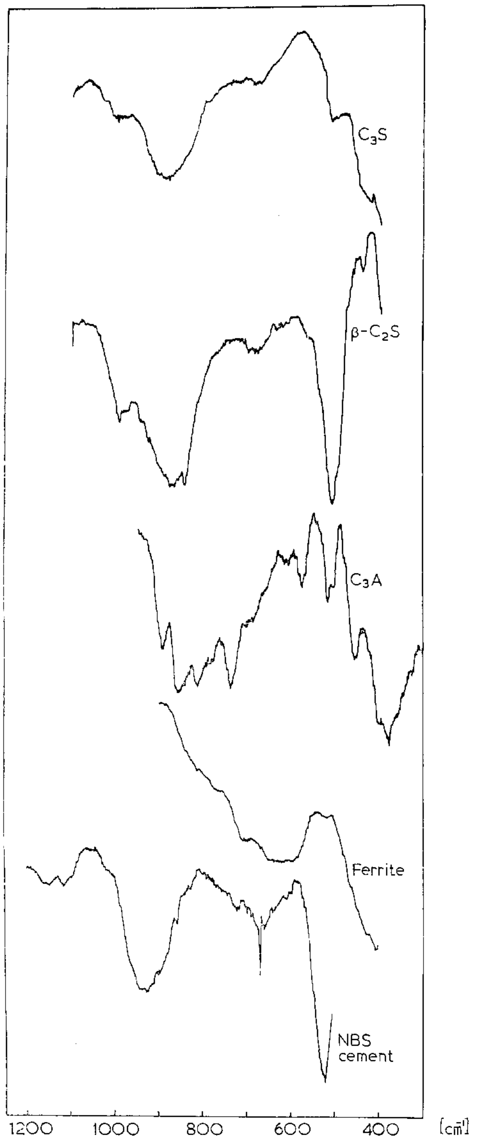

Figure 5 Reflection spectra of cement minerals and cement.

assessing the formation of relative proportions of tricalcium and dicalcium silicates in cement clinker. In this regard the overall shape of the spectral range 1000 to 800 cm^{-1} is important. A broad band with a discernible shoulder around 850 cm^{-1} usually indicates higher proportions of belite whereas mainly alitic clinkers and cements show narrow band with a peak in the range 950 to 900 cm^{-1}.

2. In the complex spectra of cement or clinker the presence of C_3A can be detected by appearance of spectral bands in the range 750 to 700 cm^{-1} but no characteristic band or spectral range could be established for the aluminoferrite phase.

3. A possiblity of assigning the appearance of a shoulder at 565 cm^{-1} to partial conversion of β- into γ–C_2S may be indicated. This, however, has to be further substantiated by experimental data.

4. Attenuated total reflection spectra of cement show better resolution and hence the reflectance technique may be more effectively employed in the routine analysis of cement and allied materials.

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