

spectrum, *d*. TLC spot). There is additionally an alkane in the extract that might be a low molecular polyethylene or a crystalline paraffin wax (*b*. TLC spot, *a*. reference spectrum of polyethylene).

The next extract (Figure 2) contains a paraffin oil made out of a foil of Opanol®. The sharp lines have disappeared (*a*. TLC spot, *b*. reference spectrum paraffin oil). The same plasticizer as in the first extract was used in this polymer (*c*). Di(2-ethylhexyl) phthalat is a product with a wide applications range.

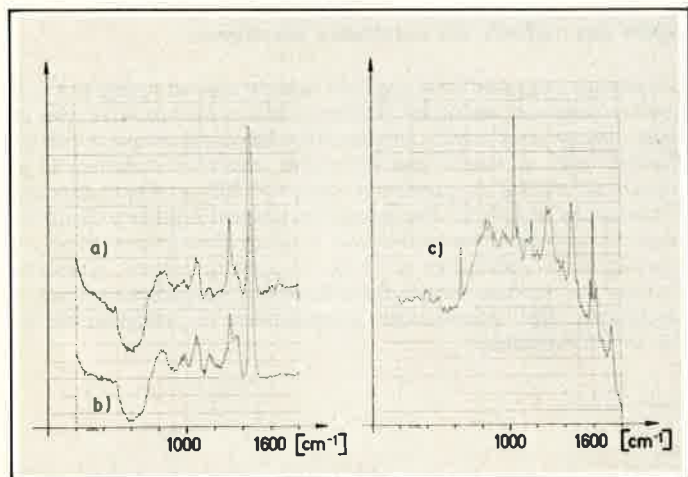


Figure 2.

The analysis of a waterhose is shown in figure 3. Besides the paraffin oil (*e*), Mesamoll® can be identified. The chemical formula is given. As it consists of molecules with different chain lengths $(CH_2)_n$, a thin layer chromatographic separation takes place. Having mainly used

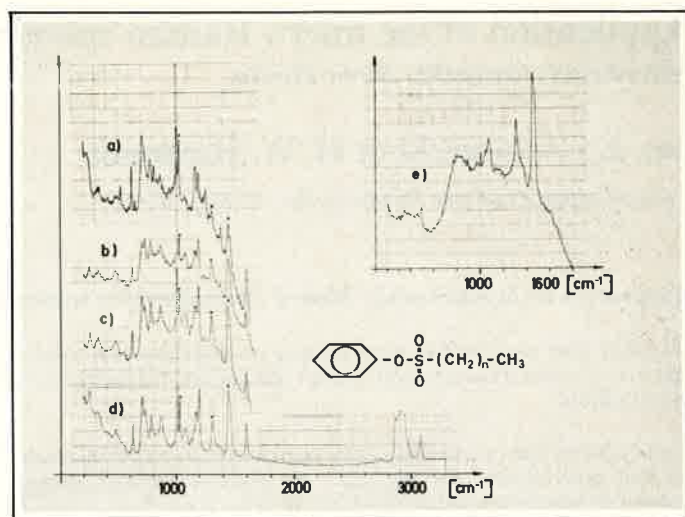


Figure 3.

petrolether as an eluent solvent, molecules with increasing chain lengths therefore moved faster. Mesamoll® can be detected in different spots on the TLC plate (*a-c*. TLC spots, *d*. reference spectrum Mesamoll®). The changes in the spectra are caused by various chain lengths.

It has thus been shown that Raman spectroscopy with the Mole can be applied to the analysis of TLC fractions down to low concentrations. We believe it is a powerful and versatile tool highly suitable to use along with other techniques (GC-MS and IR). We will be adopting this method to study problems such as aging of additives, additives in oil and plastics, and extracts of matrix materials of unknown fiber compound preprags.

Some possibilities of Raman microprobe in cement chemistry

par M. Conjeaud et H. Jaeschke-Boyer *

(Lafarge, Laboratoire de recherches, 78190 Trappes et * Jobin et Yvon, Laboratoire d'application, 91150 Longjumeau, France)

Quelques possibilités de la microsonde Raman en chimie des ciments.

La microsonde Raman a été utilisée avec succès pour obtenir les spectres Raman in situ de cristaux d'alite et de belite dans deux clinkers industriels. Des différences importantes ont été observées, et celles-ci sont comparées à la composition chimique de ces alites et belites donnée par la microsonde électronique.

L'étude des deux autres phases des clinkers (C_3A et alumino-ferrites de calcium) et celle de l'hydratation ont été abordées. L'application de

la microsonde Raman pour le C_3A et les alumino-ferrites de calcium semble peu intéressante (du fait de l'influence néfaste du fer présent dans le C_3A des clinkers). Par contre, malgré les difficultés rencontrées dans l'étude de l'hydratation, les quelques résultats obtenus montrent que la microsonde Raman devrait permettre d'obtenir des informations sur les hydrates formés lors de la prise des ciments qu'aucune autre méthode ne peut fournir.

This paper relates the results obtained in cement chemistry and published in a cement specialized review (1).

Expérimental

Samples and preparation

Small samples (100 mg are largely sufficient) of pure C_3S , β - C_2S , C_3A , C_6A_2F , C_6AF_2 and C_2F * were prepared by high temperature synthesis.

For β - C_2S only, 1% B_2O_3 by weight, was used as a stabilizing agent.

* $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$

Two industrial clinkers were studied: one a special white cement clinker, the other ordinary portland cement clinker.

In order to be able to obtain Raman spectra of alite, belite **, C_3A and calcium aluminoferrite in these clinkers, polished sections were prepared.

In order to study calcium silicate hydrate (C-S-H) three types of samples were prepared:

1. synthetic C-S-H (1) at $C/S = 1$ obtained by chemical reaction in solution between Na_2SiO_3 and CaO , and extensive washing to eliminate Na_2O (< 1% by weight remaining).

** alite and belite are the name given respectively to the impure C_3F and C_2F present in a clinker.

2. pure C_3S hydrated for 11 days in solution (water/ C_3S = 10) at 60 °C.
3. paste of ordinary portland cement hydrated for 7 weeks at water/cement ratio of 0.5.

In the latter case, a polished section was prepared as for the clinkers.

For the present work, only one of the possible modes of the Mole was used : the spectrometer Raman mode.

Results and discussion

We have limited our study to some possibilities offered by the Raman microprobe and have thus attached principal importance to the symmetric stretching vibration of SiO_4 which occurs between 800 and 900 cm^{-1} .

C_3S and alite

Pure triclinic C_3S sample shows four main lines, very well separated at 813, 845 and 885 cm^{-1} (figure 1). The line of highest intensity is at 845 cm^{-1} which is characteristic of C_3S . The lines at 813 and 885 cm^{-1} appear as satellites. Four other satellites of smaller intensity can be distinguished at higher frequencies, in agreement with Handke (2).

The Raman spectrum of monoclinic alite present in the white clinker sample is shown on figure 2. As could be expected, because of disorder introduced by foreign ions present in this alite (see table 2), the broadening of silicate lines is observed : all four C_3S lines are just apparent. The maximum remains 845 cm^{-1} , but a new line, with nearly the same intensity is detected at 832 cm^{-1} . This is not likely to

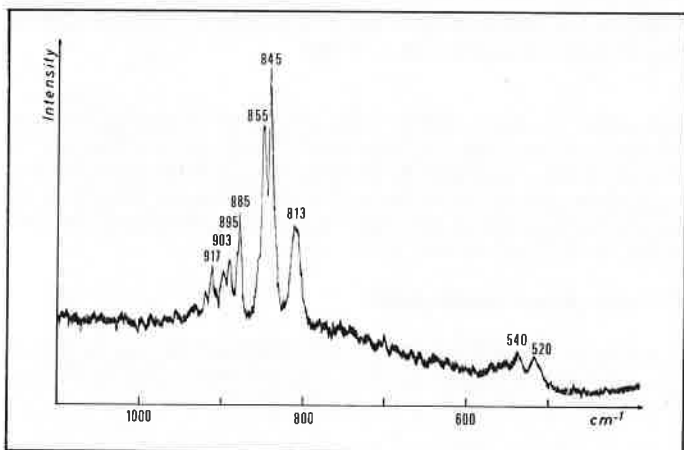


Figure 1. Raman spectra of pure triclinic C_3S

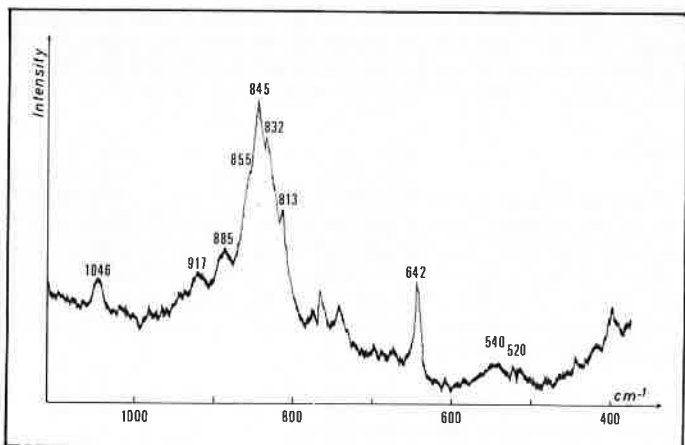


Figure 2. Raman spectra of alite in white cement (size of analysed crystal : 5 × 6 μm).

belong to the allotropic form of this alite (monoclinic), because our Raman spectrum of a synthetic monoclinic C_3S does not show 832 cm^{-1} line.

It is possible that a better structural order is associated with larger crystals. Thus, we selected alite crystals in the white clinker of very different sizes and shape (more or less elongated) and measured their spectra. No significant differences were detected, except perhaps for a slight increase in the general intensity of lines with increasing crystal size.

Turning to alite in ordinary Portland cement clinker (figure 3) further broadening of the silicates lines, as might be expected considering the larger quantity of foreign ions present, did not occur (see table 1).

Table 1. Foreign ions present in alite

	% present in alite of :	
	white clinker	ordinary Portland clinker
Fe	0.06	0.34
Al	0.4	0.54
Mg	0.3	0.68
S	0.03	0.02
K	< 0.05	1.49
Na	< 0.05	0.12

However, we observed :

1. an intensification of the 832 cm^{-1} « alite » line which becomes the strongest line in the spectrum.
2. a very strong background with a maximum around 750 cm^{-1} .

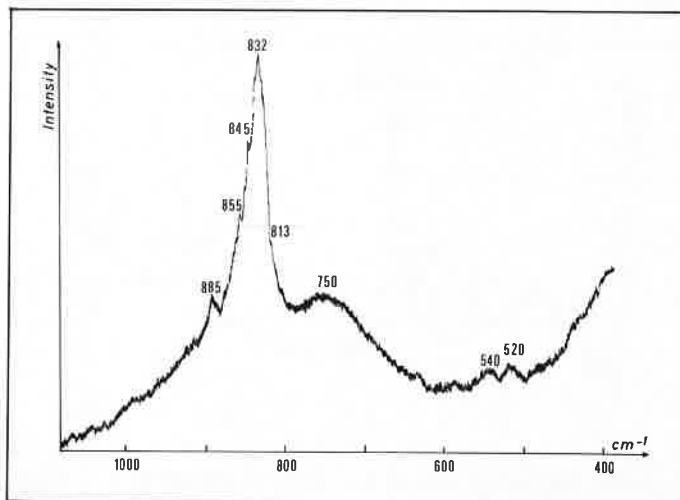


Figure 3. Raman spectra of alite in ordinary Portland cement (size of analysed crystal : 6 × 13 μm).

The same difficulty of explaining the appearance of the 832 cm^{-1} line remains. Once again it cannot be due to an allotropic effect, since alite in this clinker is rhombohedral, and a spectrum recorded on a synthetic rhombohedral alite does not show this line.

Nor is the appearance of the 832 cm^{-1} line due to a simple disorder effect because we examined a spectrum of highly ground pure C_3S . It shows very strong line broadening : the four $\nu_1 - SiO_4$ lines are no longer visible, but the maximum remains at 845 cm^{-1} (figure 4).

By contrast, the reason for the appearance of a broad band with a maximum near 750 cm^{-1} is easier to explain. It is certainly due to the Fe^{3+} present in alite in ordinary Portland cement.

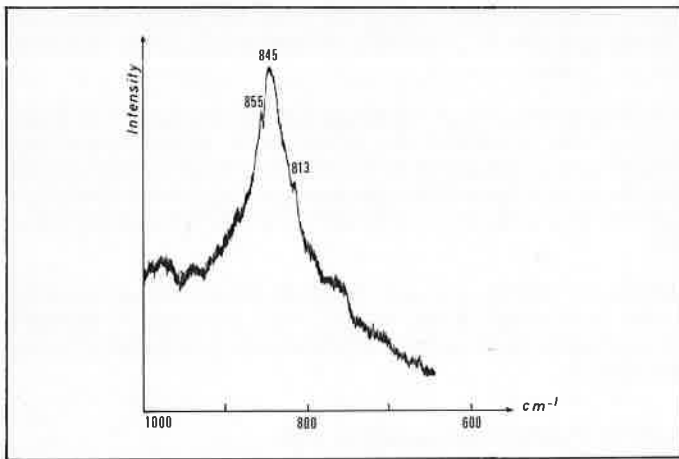


Figure 4. Raman spectra of pure triclinic C_3S after intensive grinding

A further check was made on the effect of crystal size on the Raman spectrum for alite. Apart from a general increase in intensity of lines with increasing crystal size (as observed with the white clinker) no other significant effect was evident.

C_2S and belite

The Raman spectrum of our sample of $\beta - C_2S$ stabilized by 1% B_2O_3 is shown in figure 5. It is in very good agreement with the one given by Handke. (3). The main lines ($\nu_1 - SiO_4$) are the same as for C_3S : 848 and 860 cm^{-1} which is characteristic of $\beta - C_2S$.

The belite in the white clinker, in spite of foreign ions which it contains (see table 2) gives a spectrum very similar to $\beta - C_2S$ stabilized by B_2O_3 . The 860 cm^{-1} line remains the line of highest intensity and the line broadening is very slight; the main lines remain

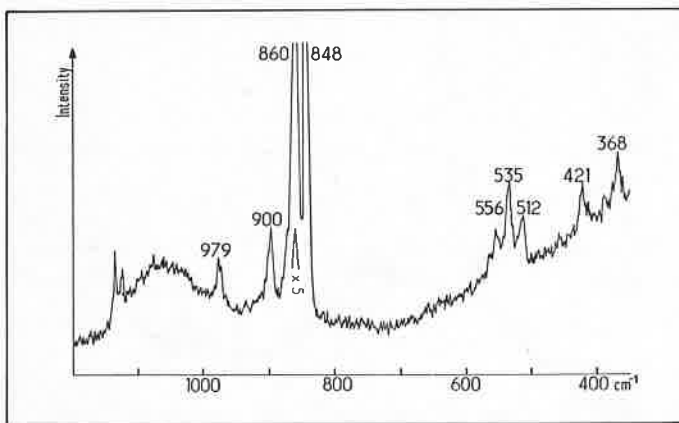


Figure 5. Raman spectra of $\beta - C_2S$ stabilized by 1% B_2O_3

Table 2. Foreign ions present in belite of the two clinkers

	% present in belite of :	
	white clinker	ordinary Portland clinker
Fe	0.12	0.66
Al	1.0	0.95
Mg	0.13	0.33
S	0.05	0.05
K	0.23	1.49
Na	0.14	0.12

well separated. Only in some of the crystals analysed was the simultaneous disappearance of $\nu_4 - SiO_4$ triplet (556, 535, 512 cm^{-1}) and the 900 cm^{-1} line noticed.

As could be expected from the much larger quantity of foreign ions present, the Raman spectra of belite in ordinary Portland cement are much more affected (figure 6). We observe :

1. strong broadening of silicate lines which are not always separated, and a decrease of the 860 cm^{-1} line, which reduces to the same height as the 848 cm^{-1} line. Such a transformation can be attributed to disorder, since the same effect was found after strongly grinding $\beta - C_2S$ stabilized with B_2O_3 .
2. a very strong background with a maximum at 740 cm^{-1} . This band can be attributed to the presence of Fe^{3+} in the structure.

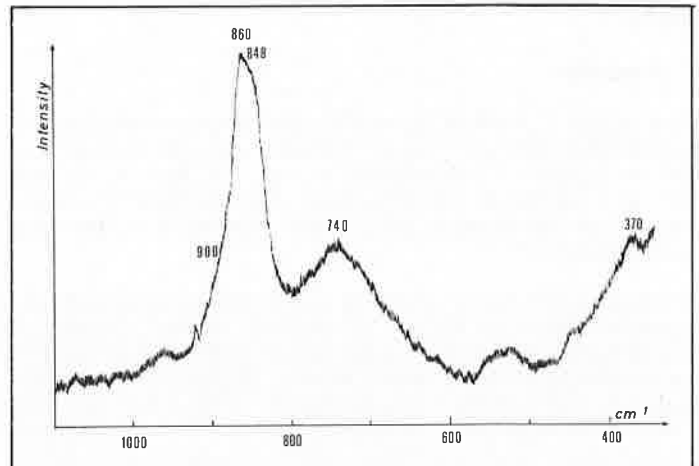


Figure 6. Raman spectra of belite in ordinary Portland cement (size of analysed crystal : 15 x 15 μm)

As for alite, we did not find for belite a significant difference between different sized or shaped crystals, either in white cement clinker, or in ordinary Portland clinker. By contrast, it must be pointed out that the Raman spectra show for C_2S a much smaller sensitivity to impurities effects than C_3S , result which confirms what was obtained by I.R. on synthetic $\beta - C_2S$ (4).

C_3A and calcium alumino-ferrite

C_3A exhibits a simple spectrum, with fine lines, wherein the line at 761 cm^{-1} corresponds to the stretching vibration of the Al-O bond and the line at 508 cm^{-1} correspond to its deformation (5).

Calcium alumino-ferrite spectra show only broad bands with maxima around 750 cm^{-1} although the samples used were well crystallized as verified by X-ray diffraction.

Relatively few spectra were recorded for C_3A in clinker, because the quantity of Fe^{3+} in solid solution (which reaches 2% even in white clinker) produces a result very similar to the alumino-ferrite spectrum with a single large band centered on 750 cm^{-1} .

C-S-H

The Raman spectrum of synthetic C-S-H (1) at C/S = 1 exhibits only one line rather broad and not very strong, at 670 cm^{-1} (figure 7). It is probably due to the symmetric stretching motion of the Si-O-Si bridges (6). And it occurs at the same energy as in the rankinite $Ca_3Si_2O_7$. This observation suggests the possibility that C-S-H (1) contains mainly pyrosilicate groups ($Si_2O_7^{5-}$) as found by Gard and Taylor (7) for C-S-H (7).

The absence of Si-O stretching frequencies should be compared with what is observed for sheet silicates (8).

C-S-H (7) Raman spectra obtained from powdered hydrated C_3S were not exploitable. Only one weak line at 850 cm^{-1} appeared on

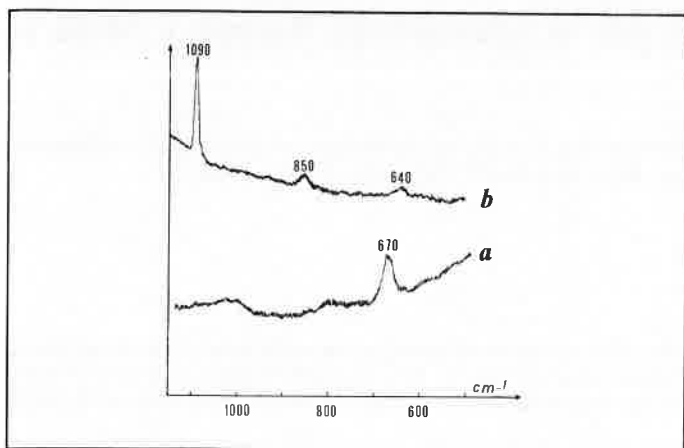


Figure 7. Raman spectra of two C-S-H :

- (a) synthetic C-S-H (1)
 (b) type III C-S-H in a cement paste

some spectra. It corresponds to the symmetric stretching vibration of SiO_4 . But it is probably due to unhydrated C_3S , included in the analysed volume, although the C-S-H coating on the C_3S grains must be rather thick (— 1 — 2 μm), after 11 days hydration at 60°.

In order to avoid this problem, we analysed C-S-H directly in a cement paste, sufficiently aged (7 weeks) to have a substantial coating of C-S-H around the cement grains. Then, by examining a polished section of this cement paste, it was possible with the Raman microprobe to focus the laser beam onto the C-S-H alone. However, even under these conditions, we could only obtain the spectrum shown in fig. 7, with a 850 cm^{-1} line which cannot be attributed with certainty to C-S-H, since it might be due to subjacent C_3S .

The 1090 cm^{-1} line being a carbonation line, the only line which belongs undoubtedly to the C-S-H is the 640 cm^{-1} line. It occurs in the Si-O-Si symmetric stretching region. But a displacement with respect to the synthetic C-S-H (1) is observed. It might be due to additional Ca, Al and Fe present in C-S-H from hydrated cement paste. But it is worth notice too that the same displacement is observed for β -wollastonite $\text{Ca}_3\text{Si}_3\text{O}_9$. This suggests that the analysed C-S-H (most probably type III C-S-H, because of the age of the sample and since we always focussed the laser beam as next to unreacted cement grains as possible) contains mainly $\text{Si}_3\text{O}_9^{6-}$ anions. And this result is in good agreement with those obtained by trimethylsilylation (9).

Again the absence of Si-O stretching frequencies should be compared with what is observed for sheet silicates (8). But the weakening of spectral bands observed with C-S-H in hydrated cement paste should be attributed also to the poor crystallinity of this C-S-H, as evident from X-ray diffraction.

Conclusion

The Raman microprobe has been applied successfully to the study of individual crystals of calcium silicates, both in white and gray

Portland cements. Important differences were detected between the two clinkers. Raman spectra of alite and belite in the white cement differ relatively little from pure phases. On the other hand, although belite absorbs more impurities in its structure than alite, Raman spectra of alite are more affected by impurities in both cements than belite spectra.

The Raman microprobe thus opens a new route, to direct information on structure and crystallinity of alite and belite in clinkers. Much may be learned by this technique, especially in conjunction with electron microprobe, about the influence of raw materials composition, firing and cooling of clinker... on alite and belite. It must also be pointed out that none of the problems encountered with gray Portland cements using standard Raman spectroscopy (10) arose in this study.

By contrast, the study of C_3A and calcium aluminoferrites in cement with the Mole does not seem very rewarding, because of the damping effects of iron in solid solution.

A more optimistic view may be taken for hydrate study. It is not as straightforward as it is for anhydrous silicates. More work must be done to find out the best conditions to enhance spectra. But afterwards, the Raman microprobe will give information on structure of C-S-H in hydrated cement paste on a crystal chemical scale with up to-day was impossible to obtain (for example about « inner » and « outer » hydration products). Furthermore, it is interesting to point out, especially for hydrate study, that all experiments can be performed under any desired atmosphere, neither vacuum nor conductive coating being needed as in electron microprobe.

Finally, it must be said that only some applications of the Raman microprobe in cement chemistry were explored, we did not look, for example, at admixtures or carbonation nor at the possibility of differentiating between thaumasite and ettringite in a hydrated cement paste or mortar, all areas in which the Raman laser microprobe could be very useful.

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