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HYDRATION OF CEMENT MINERALS WITH VARIOUS ADMIXTURES STUDIED BY DIFFERENTIAL THERMAL ANALYSIS AND INFRARED SPECTROMETRY

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ABSTRACT

A thermal analysis study of the effect of $CaCl_2$, CdI_2 and $CrCl_3$ on the hydration reaction of $3CaO \cdot SiO_2$ (C_3S) was performed. The model suggested is derived from both the thermoanalytical studies and the infrared spectra.

INTRODUCTION

The hydration of Ca_3SiO_5 (C_3S) with $CaCl_2$, CdI_2 and $CrCl_3$ as admixtures, reported here, was studied by differential thermal analysis (DTA) and infrared spectrometry (IR). Both methods allow the follow-up of the hydration process for periods varying from one day onwards.

The thermal behavior of hydrated C_3S alone[1,2] and with varying amounts of $CaCl_2$[3,4] has been reported by Ramachandran. C_3S exhibits a reversible transition at about 915°C, from which the degree of hydration could be estimated. The accelerating effect of $CaCl_2$ was also demonstrated using this technique, but it was shown that different amounts of $CaCl_2$ affect the hydration rate differently at different stages of hydration. For thirty days the extent of hydration in terms of estimated $Ca(OH)_2$ was in the order: $C_3S+1\%\ CaCl_2 > C_3S+0\%\ CaCl_2 > C_3S+4\%\ CaCl_2$. It was shown later[5] that the optimal percentage of $CaCl_2$ was 2%. Skalny et al.[6,7] studied the addition of both $CaCl_2$ and alkali carbonate on the hydration of cement minerals. While the DTA curves of C_3S before hydration are comparatively complex[1], those for hydrated C_3S are simple, showing in fact, two prominent peaks: one for the dehydration of CSH**, at lower temperature and the other for $Ca(OH)_2$, at higher temperature.

Infrared spectroscopy finds an extensive use in qualitative analysis of organic compounds. Recently, this method has been adapted for studies on morphological structure of minerals, and can be used for the analysis of cement minerals and Portland cement, and for the study of the development of the corresponding hydration products.

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**CSH = calcium silicate hydrate (tobermorite gel).

Midgley[8–10] has shown that the IR absorption spectra of the main constituents of Portland cement were well established and sufficiently different to allow analysis. These IR curves, published for the first time, were similar to those which had been found by Hunt[11]. A similar study was recently reported by Henning and Kaessner[12].

Data for cement minerals were reported by Lehmann and Dutz[13], Lazarev[14], Roy[15], Paredes et al.[16] and Vazquez[17]. Baron and coworker[18] studied hydrated cements and clays, concentrating on the water and hydroxyl vibrations, and Cornell and Cotte[19] measured the moisture content of cements, using IR.

The aim of this work was to study the effect of various inorganic salts as admixtures on the hydration of C_3S both by DTA and IR.

EXPERIMENTAL

Materials

A stoichiometric mixture of $CaCO_3$ (Analytical Reagent, Malinckrodt) and precipitated SiO_2 (BDH Laboratory Reagent) was repeatedly heated to 1550°C until C_3S containing practically no free CaO (by X-ray analysis) was obtained. The C_3S was milled to pass a 200 mesh sieve and had a surface area of 1330 $cm^2\ g^{-1}$ (Blaine method).

β-C_2S was obtained in a similar way, by heating the stoichiometric mixture of $CaCO_3$ and SiO_2 to 1500°C for 24 h. The formation of γ-C_2S was avoided by adding small amounts of Na_2CO_3 to the mixture before heating. The admixtures used were: $CaCl_2$, CdI_2, and $CrCl_3$ (A.R. BDH Laboratory Reagents).

Preparation of samples

5 g of silicates were treated with 2.5 ml of the appropriate solutions, and with pure water (for comparison) at a temperature of 22°C (±1). The pastes obtained were separated into different vials which were tightly stoppered and kept at a temperature of 22°C (±1).

The hydration process was stopped at various stages, by breaking the "stone", grinding it and washing the powder obtained, several times, with cold acetone and storing it under vacuum. The solutions for hydration were 0.36 M of $CaCl_2$, $CrCl_3$ and CdI_2.

Methods of investigation

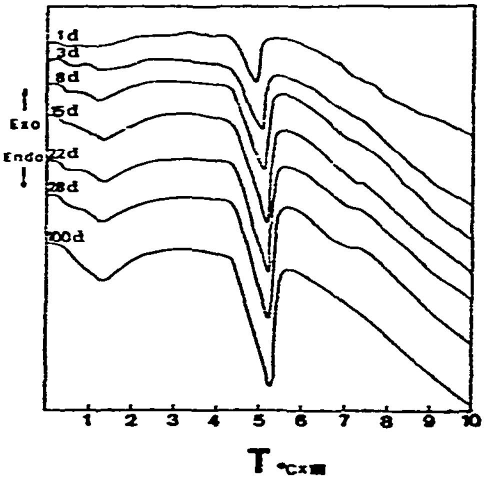
DTA curves were obtained by a Mettler thermoanalyzer 1. The rate of heating was maintained at 10°C min^{-1} from ambient temperature to 1000°C in a stream of dry nitrogen (5 l h^{-1}). The weight of each sample was approximately 200 mg. The sensitivity was 50 μV/recorder span.

The KBr disk method was used for IR, 2 mg of the sample were ground with 200 mg of dried KBr and the disks were produced by vacuum die and under a pressure of 9 ton cm^{-2}.

A Perkin-Elmer 457 grating infrared spectrophotometer was used, with a pure KBr disk in the reference beam.

RESULTS AND DISCUSSION

There are two points to stress when discussing the DTA curves. First, there are two endothermic peaks in the thermogram of hydrated cement mineral: the dehydration of CSH shown by a broad shallow band peaking at ca. 130°C for all samples, and the dehydration of $Ca(OH)_2$ which is given by a sharp peak at ca. 500°C. Second, the dehydration of $Ca(OH)_2$ does not appear at a constant temperature but shifts to higher temperatures with age. This shift is closely associated with the degree of hydration; the higher the degree of hydration, the higher the temperature in which $Ca(OH)_2$ decomposes. In the neat sample (Fig. 1) the run for 5 h shows a peak at 445°C which shifts to 490°C after one day and continues to shift, reaching 520°C after 22 days (remaining constant thereafter). In the C_3S with $CaCl_2$ as admixture (Fig. 2) the peak reaches 510°C already after one day, thus displaying an advanced stage of hydration, and shifting to ~520°C after 28 days.



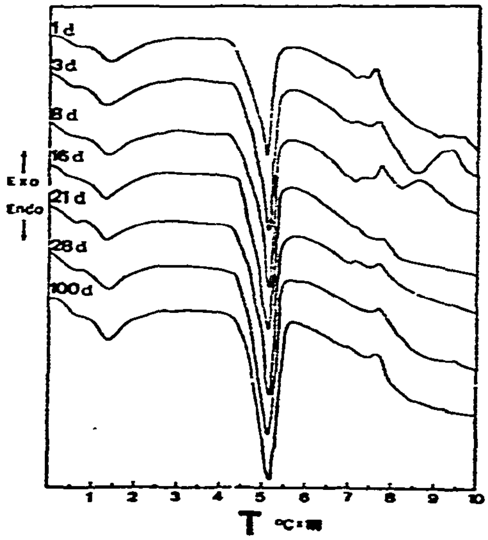
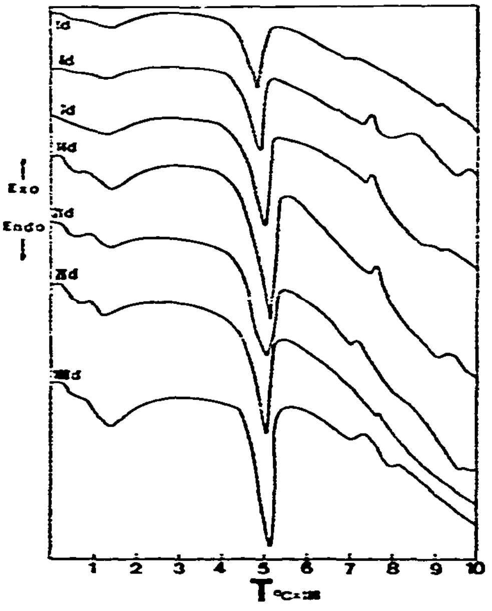


Fig. 1. Thermogram for neat C_3S–H_2O system.

Fig. 2. Thermogram for C_3S–$CaCl_2$–H_2O system.

This dramatic phenomenon has hitherto not been reported in thermal studies dealing with cement. The behavior of CdI_2 and $CrCl_3$ is similar (Figs. 3 and 4): a shift from an initial 475°C in CdI_2 and from 480°C in $CrCl_3$ which also reaches ~520°C. Thus, both CdI_2 and $CrCl_3$ appear to accelerate the hydration as compared to the neat C_3S but $CaCl_2$ surpasses them all. This technique enables a fast and neat method for detecting semi-quantitatively the effect of various admixtures, on the development of the hydration reaction. This phenomenon cannot be explained only on the basis of the higher *content* of $Ca(OH)_2$ for the different ages, because the peak remains constant after ~22 days and does not continue to shift although more $Ca(OH)_2$ is being formed. We would like to suggest that the effect may also be connected with the existence of differently bonded forms of the $Ca(OH)_2$: for short hydration periods, the $Ca(OH)_2$ forms on the surface of the C_3S particles and with time it diffuses into the bulk. A higher temperature is needed to decompose this "bulk" $Ca(OH)_2$.



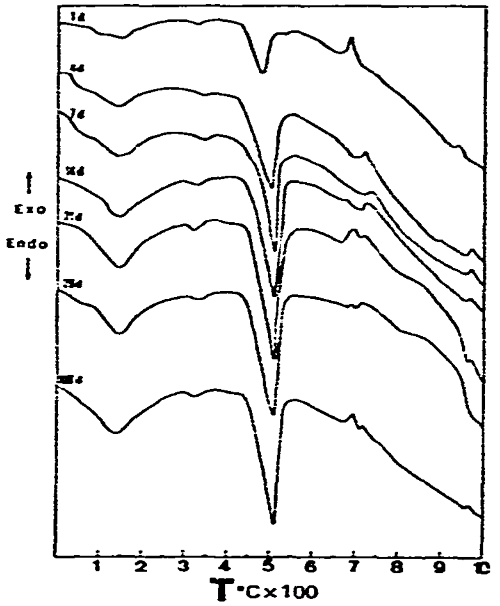


Fig. 3. Thermogram for C_3S–CdI_2–H_2O system.

Fig. 4. Thermogram for C_3S–$CrCl_3$–H_2O system.

The two dry minerals: β-$2CaO \cdot SiO_2$(β-C_2S) and $3CaO \cdot SiO_2$(C_3S) show no IR absorption between 4000–2000 cm^{-1} thus proving their complete initial unhydrated state. In the valency vibration region, 1000–800 cm^{-1}, there is a difference between the two minerals: both show a wide complex absorption exhibiting four maxima but those for C_3S are located at lower wave numbers; the deformation vibrations, practically the same, are located at ~510 cm^{-1} for β-C_2S and at ~515 cm^{-1} for C_3S.

After hydration two main regions of absorption clearly appear: the $Ca(OH)_2$ and associated OH vibrations at ~3650 cm^{-1} and the SiO_4 regions 1000–800 and ~500 cm^{-1}. In comparison to the dry β-C_2S one sees the appearance of the "OH" already after 5 h of hydration and its growth with time up to 8 days, its maxima being located at ~3640 cm^{-1}. Overlapping with this sharp band there appears a broad one due to associated "OH" in the region 3700–3200 cm^{-1}. Further hydration of β-C_2S to 28 days does not materially change the picture. Simultaneously with the formation of $Ca(OH)_2$ there is some formation of $CaCO_3$ (broad shallow absorption 1500–1400 cm^{-1}). Both the valency and the deformation vibrations show a loss of intensity[13] with the progress of hydration (Figs. 5a and b). On the other hand, there is a

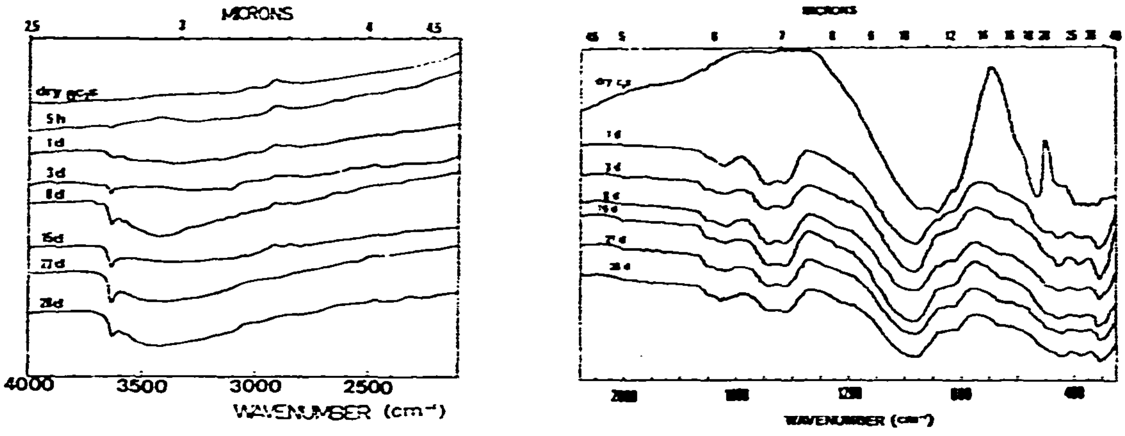


Fig. 5. IR spectra of β-C_2S–water system. (a) 4000–2000 cm^{-1}. (b) 2000–250 cm^{-1}.

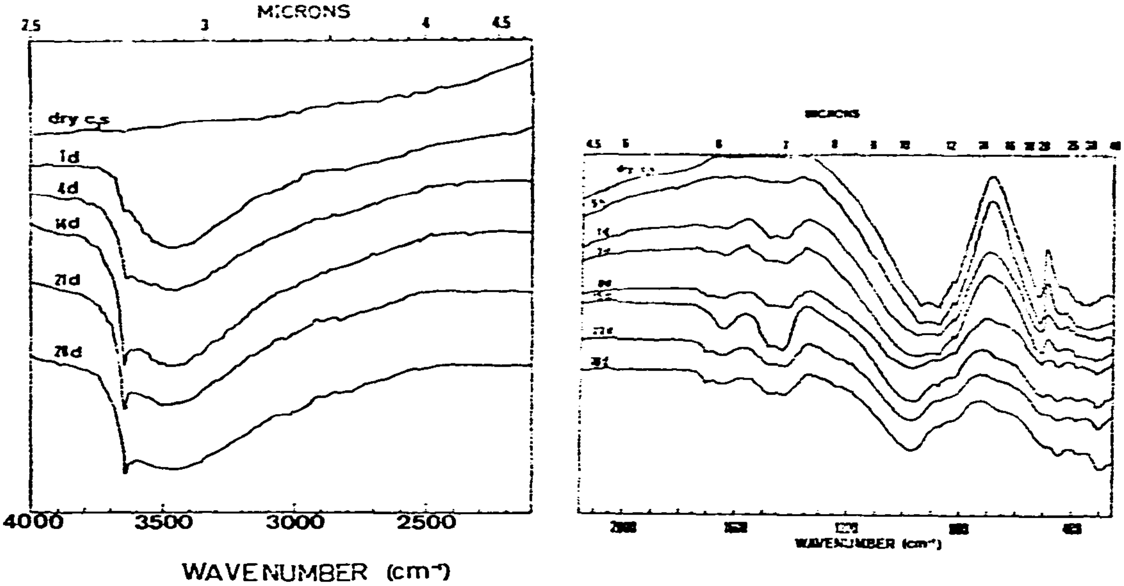


Fig. 6. IR spectra of neat C_3S–water system. (a) 4000–2000 cm^{-1}. (b) 2000–250 cm^{-1}.

continuous growth of the $Ca(OH)_2$ band for the hydration of C_3S with age (Fig. 6a). Near the $CaCO_3$ region, the appearance of the deformation vibration (ν_2) of the H_2O at ~1640 cm^{-1} can be seen in contrast to its only very vague appearance in the hydrated β-C_2S, and thus shows the much slower hydration of β-C_2S. In the valency region one sees two effects: the loss of intensity coupled with a shift of the maxima to longer wave numbers.

These effects are caused by the low crystallinity of the C–S–H gel formed and the association of the initial SiO_4 tetrahedra to larger structures. The loss of intensity of the deformation band-region is far more noticeable here than for β-C_2S (Fig. 6b).

These results, concerned with the hydration products, are in good accord with results obtained in this laboratory using SEM techniques[20].

The influence of various inorganic salts on the hydration of C_3S was studied by many other techniques (DTA, TG, SEM and strength development) and it was useful to study this phenomenon by IR as well. For all three admixtures used, the $Ca(OH)_2$ and associated "OH" bands appear, being especially intense in the case of $CaCl_2$. A clear sharp $Ca(OH)_2$ band appears after 1 day (for $CaCl_2$) and the associated broad

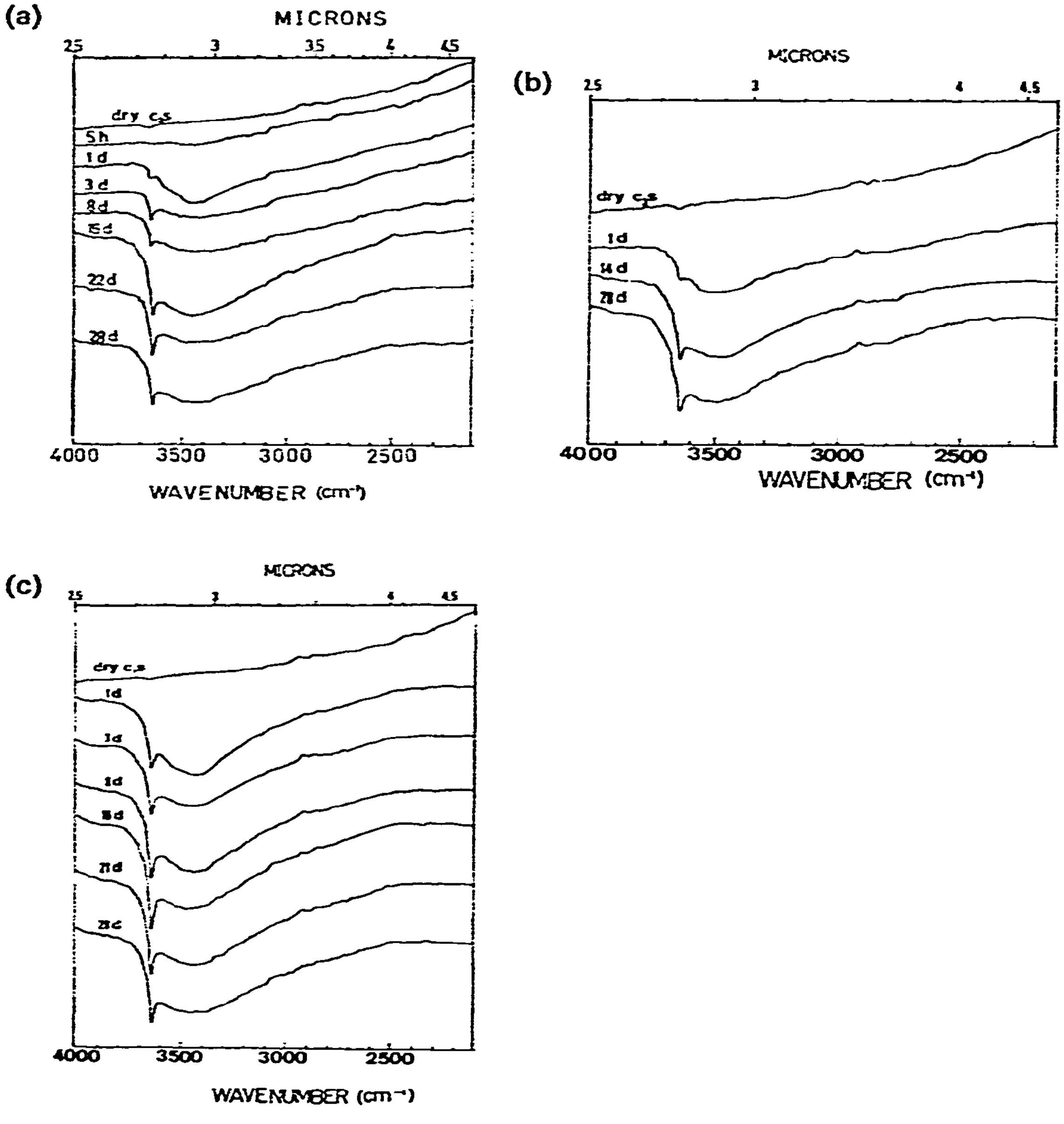


Fig. 7. IR spectra 4000–2000 cm^{-1}. (a) C_3S–$CaCl_2$–water system. (b) C_3S–CdI_2–water system. (c) C_3S–$CrCl_3$–water system.

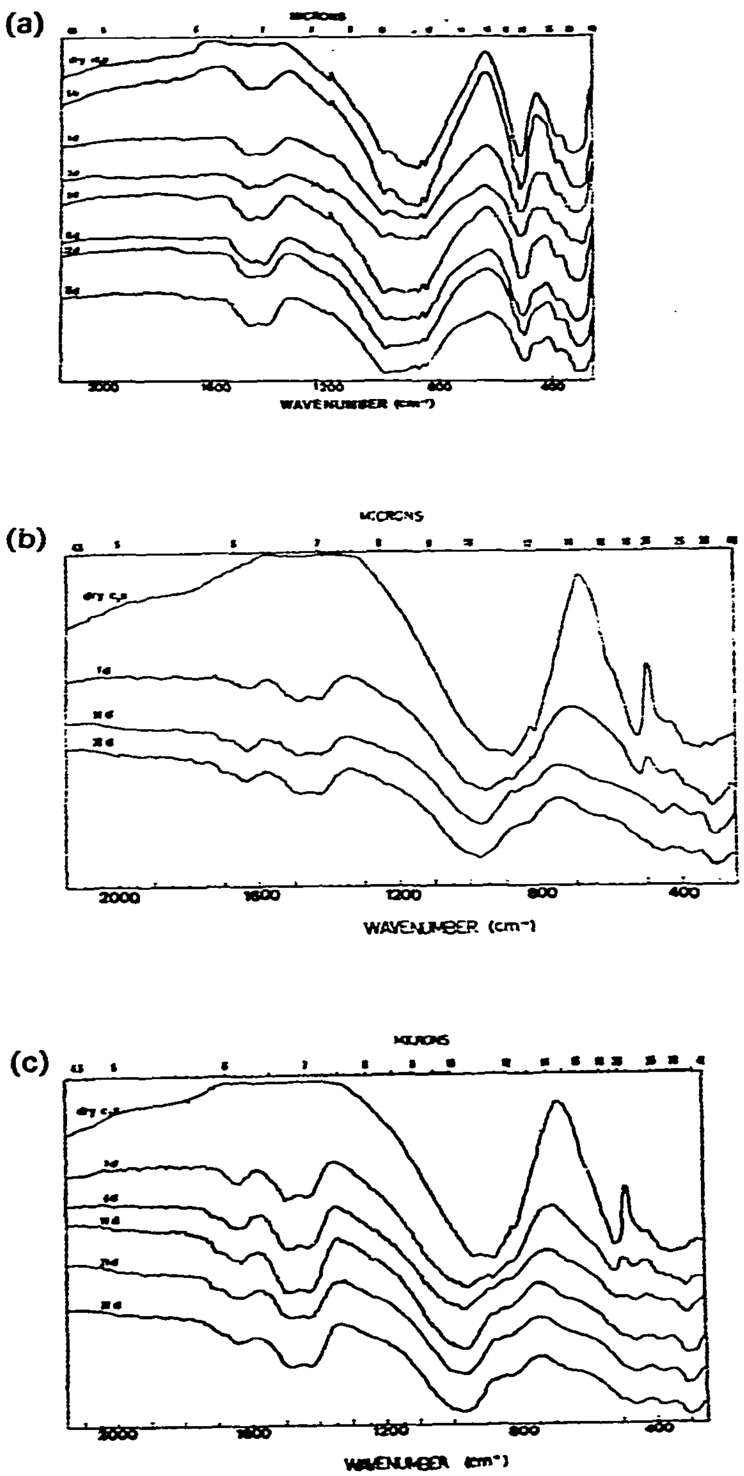


Fig. 8. IR spectra 2000–250 cm^{-1}. (a) C_3S–$CaCl_2$–water system. (b) C_3S–CdI_2–water system. (c) C_3S–$CrCl_3$–water system.

"OH" band is more intense for the samples with admixtures as compared to the neat mineral (Figs. 7a–c). In the second region, a similar effect of loss of intensity and shift of location of the SiO_4 bands seen for the neat C_3S is apparent (Figs. 8a–c). The maxima for neat dry C_3S is located at $\sim$935 cm^{-1} and it shifts to $\sim$975 cm^{-1} for all the samples after 28 days hydration. After one day's hydration, however, the maxima for neat C_3S is barely shifted; on the addition of CdI_2 and $CrCl_3$ it is shifted to $\sim$950 cm^{-1} while the addition of $CaCl_2$ shifts the maxima to $\sim$965 cm^{-1}. This phenomenon again demonstrates the well-known accelerating effect of $CaCl_2$ on the hydration of cement minerals and Portland cement.

In conclusion, DTA and IR afford simple and reliable methods for evaluating the effect of various inorganic admixtures on the hydration process of cement minerals. The model for the structure of $Ca(OH)_2$, derived from DTA, is complementary to the model for the structure of the C–S–H as derived from IR.

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REFERENCES

1 V. S. Ramachandran, *J. Therm. Anal.*, 3 (1971) 181.
2 V. S. Ramachandran, *Therm. Anal. 3rd ICTA*, 2 (1972) 255.
3 V. S. Ramachandran, *Thermochim. Acta*, 2 (1971) 41.
4 V. S. Ramachandran, *Mater. Constr.*, 4 (1971) 19.
5 V. S. Ramachandran, *Thermochim. Acta*, 3 (1972) 343.
6 J. Skalny and I. Odler, *Mag. Concr. Res.*, 19 (1967) 203.
7 J. N. Maycock and J. Skalny, *Thermochim. Acta*, 8 (1974) 167.
8 H. G. Midgley, *Chemistry of Cement, Proc. 4th Int. Symp., Washington*, Nat. Bur. Stand. Monogr. 43, U.S. Department of Commerce, 1960, p. 479.
9 H. G. Midgley, *D.S.I.R. Building Research Station Note*, D8 11, 1962.
10 H. G. Midgley, in H. F. W. Taylor (Ed.), *The Chemistry of Cements*, Vol. 1, Academic Press, London, 1964, ch. 3, p. 89.
11 C. M. Hunt, University of Maryland, *Doctoral Dissertation*, 1958.
12 O. Henning and B. Kaessner, *Epitoanyag*, 23 (1971) 414.
13 H. Lehmann and H. Dutz, *Chemistry of Cements, Proc. 4th Int. Symp., Washington*, Nat. Bur. Stand., Monogr. 43, U.S. Department of Commerce, 1960, p. 513.
14 A. N. Lazarev, *Opt. Spektrosk.*, 9 (1960) 195.
15 D. M. Roy, *J. Amer. Ceram. Soc.*, 41 (1958) 293.
16 P. G. de Paredes, J. Calleja, T. Vazquez and J. L. Cebrian, *Mater. Constr., Ultimos avances*, 136 (1969) 17.
17 (a) T. Vazquez, *Monogr. I.E.T.cc.*, 297, Madrid (1971).
(b) T. Vazquez, *Cuad. Investig. I.E.T.cc.*, 22, Madrid (1969).
18 (a) A. Baron and R. Sierra, *Rev. GAMS*, 4 (1968) 412.
(b) A. Baron, *C.R. Acad. Sci., Paris*, 266C (1968) 49.
(c) A. Baron, *Bull. Soc. Fr. Céram.*, No. L32/D553 (1968) 73.
(d) A. Baron, *Rapport de recherche*, No. 2, Ministère de L'équipement et de logement, 1969.
19 J. B. Cornell and A. T. Cotte, *J. Appl. Chem. Biotechnol.*, 22 (1972) 455.
20 L. Ben-Dor and D. Perez, to be published.