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## INFRARED ABSORPTION TESTS ON PARTIALLY HYDRATED CEMENT PASTES AND PURE PHASES

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### Synopsis

Partially hydrated cement pastes of 4 kinds of commercial cement, which differ mainly in their  $C_3A$  contents, and synthesized pure phases of hydrated compounds were tested by an infrared absorption spectroscopic method. The IR spectra of the partially hydrated cements were almost identical to the spectrum of hydrated alite, especially at later curing ages, except for the absorption of the sulfate ion. The sulfate ion absorption decreased gradually with curing age, up to 365 days or more. This suggested that the composition of the hydrous calcium sulfoaluminate phase was changing. The decrease of  $SO_4^{2-}$  ion absorption was somewhat larger in the case of white portland cement than in the case of grey portland cement. The form of gypsum in unhydrated cement and the bonding of  $OH^-$  ion in pure phases are discussed.

### Introduction

Infrared absorption spectroscopy has been used effectively in portland cement research. Kalousek and Roy<sup>(1)</sup> (a) used IR to study the characterization of interlayer water in hydrous calcium silicates. Hunt<sup>3</sup> presented the IR spectra of silicates and aluminates related to portland cement. Lehman and Dutz<sup>4</sup> used IR to determine the rate of hydration of cements and cement compounds, and Midgley<sup>5</sup> used it for the determination of the phases in portland cement pastes. Takemoto, Uchikawa and Takagi<sup>6</sup> used it for studies of the completely hydrated cement compounds. Majumdar and Roy<sup>7</sup> studied in detail the characteristics of water molecules in some calcium aluminate hydrates.

The present paper reports IR spectroscopic studies of hydrated portland cements and hydrated portland cement compounds, and in particular demonstrates that the absorption of  $SO_4^{2-}$  ion decreases with curing age, suggesting changes in the hydrous calcium sulfoaluminates. All the tests were done to participate in the cooperative studies designed to evaluate methods for identifying hydrated phases in portland cement pastes, as sponsored by Project Committee A2E06.

### Experimental Procedure

#### Materials

The cement and partially hydrated samples of it, and the hydrated compounds, were distributed by the Subcommittee A2E06 (3) of project Committee A2E06. In addition, a Japanese white portland cement (designated as C - 4) and its clinker (designated as K - 1) were used. The chemical compositions of the cements differ mainly in their potential  $C_3A$  contents, as shown in Table 1. The method of preparation of the partially hydrated cements was reported previously in this report.

#### Measurement of Infrared Absorption Spectra

Instrument: Recording infrared spectrophotometer, triplepath and double beam type (Koken DS - 301 type of Japanese Spectroscopic Co., Ltd.)

Wave number limit: 4000 - 400  $cm^{-1}$ .

Prism: NaCl and KBr.

Condition of operation: Slit program 0.86 (10 $\mu$ ) for NaCl prism, 1.60 mm (20  $\mu$ ) for KBr prism. Suppression 8. Recording speed 7. Response 1. Gain 5.

Preparation of specimen: KBr pellet method, 8.0 mg of sample/500 mg of KBr; Nujol mull method, 25.0 mg of sample/3 drops of Nujol. Calibration of the spectrophotometer was done with reference to the polystyrene absorption peaks at 3083, 2924, 1603 and 906  $cm^{-1}$ .

## Results and Discussion

The IR spectra of an unhydrated and a partially hydrated cement, and a clinker, are shown in Fig. 1. These spectra for C -4 and K -1 illustrate typical results. The other cements showed similar results. IR spectra of the hydrated compounds are shown in Fig. 2.

### General Appearance

The general pattern of the IR spectrum of an unhydrated cement is similar to that of an unhydrated clinker, except mainly in the region of absorption of the  $\text{SO}_4^{2-}$  ion vibration from 1050 - 1300  $\text{cm}^{-1}$ .<sup>(8)</sup> The C -4 cement in Fig. 1 shows the absorption of hemihydrate with three peaks in the above region. The C-1, C -2 and C -3 cements show the absorption of gypsum which has two peaks in the above region, as illustrated in Fig. 3. The general patterns of hydrated samples of clinker and cements are similar to those of hydrated samples of alite and  $\beta\text{-C}_2\text{S}$ , especially at the later ages. In addition, the hydrated cements indicate an absorption due to the  $\text{SO}_4^{2-}$  ion vibration of hydrous calcium sulfoaluminates, as found in the 1070 - 1300  $\text{cm}^{-1}$  region.<sup>3, 4, 5, 9</sup> The large broad absorption, the peak of which is at about 920  $\text{cm}^{-1}$  in the cases of unhydrated samples of clinker and cement and at about 970  $\text{cm}^{-1}$  in the cases of hydrated samples of clinker, cement, alite and  $\beta\text{-C}_2\text{S}$ , arises from the vibrations within  $\text{SiO}_4^{4-}$  tetrahedra of calcium silicates.<sup>3, 10</sup> The difference between these two wave numbers could be due to hydration of these silicates.<sup>4</sup> The large absorption whose peak is at 3440 - 3480  $\text{cm}^{-1}$  in hydrated samples of clinker, cement, alite and  $\beta\text{-C}_2\text{S}$  is due to hydrogen bonded OH stretching vibrations, primarily in calcium silicate hydrate<sup>10</sup> (that is, C-S-H gel). The small sharp absorption at 3620 - 3640  $\text{cm}^{-1}$  in hydrated samples of clinker, cement and alite is due to OH stretching vibrations in  $\text{Ca}(\text{OH})_2$ .<sup>(3)</sup> Hydrated  $\beta\text{-C}_2\text{S}$  is considered to contain a small amount of  $\text{Ca}(\text{OH})_2$ , as indicated by a weak shoulder at the above number. The two hydrous calcium sulfoaluminates,  $\text{C}_6\text{AS}_3\text{H}_{32}$  and  $\text{C}_4\text{ASH}_{12}$  showed a large absorption at about 3450  $\text{cm}^{-1}$ , thus suggesting that they contain hydrogen-bonded OH in their structure.  $\text{C}_6\text{AS}_3\text{H}_{32}$  showed another clear peak at 3640  $\text{cm}^{-1}$ , suggesting that it contains at least two kinds of water of crystallization. This assumption is also indicated by its dehydration curve upon heating,<sup>9</sup> and by its assumed structural formula.<sup>11</sup> The hydrogen-bonded OH in C-S-H gel could be from a water molecule in the structure.  $\text{C}_4\text{AH}_{10.5}$  showed a sharp absorption at about 3650  $\text{cm}^{-1}$ , suggesting that most of its water of crystallization is due to OH<sup>-</sup> ion, without hydrogen bonding. The absorption at about 1650  $\text{cm}^{-1}$  is due to the OH bending vibrations in C-S-H gel,<sup>1</sup> in the cases of hydrated samples, or in calcium sulfate hydrate in the case of unhydrated cement.<sup>8</sup> The absorptions having double peaks in the 1350 - 1540  $\text{cm}^{-1}$  region of hydrated clinker, cement, alite and  $\beta\text{-C}_2\text{S}$  could be due to the vibration of  $\text{CO}_3^{--}$  ion, as caused by carbonation,<sup>3, 12</sup> differing from the other interpretation.<sup>5</sup>

### Decrease of Sulfoaluminate

As shown in Fig. 1, the 1070 - 1300  $\text{cm}^{-1}$  absorption of  $\text{SO}_4^{2-}$  ion in hydrated cement decreased with curing age. The absorption areas were measured by a planimeter, as shown in Fig. 3. The areas plotted against the curing ages for 4 kinds of cement are shown in Fig. 4. The areas decreased with an increase in curing age, becoming small at 365 days for all cements (especially for C -2 and C - 4, which are white portland cements). The distinct  $\text{SO}_4^{2-}$  bearing phases in hydrated cement could be the two hydrous calcium sulfoaluminates  $\text{C}_6\text{AS}_3\text{H}_{32}$  and  $\text{C}_4\text{ASH}_{12}$ .

The sulfoaluminate contents of all hydrated cements cured for 90 and 365 days were calculated from the  $\text{SO}_4^{2-}$  and  $\text{Al}_2\text{O}_3$  concentrations in the unhydrated cement and from their loss of weight upon heating the hydrated cements. The results were 7.4 to 9.6 wt. % in the case of trisulfate, and 11.1 to 14.3 wt. % in the case of monosulfate, assuming that all of the compounds containing  $\text{Al}_2\text{O}_3$  have hydrated at these ages.<sup>13</sup> Fig. 5 shows the IR spectra of the mixtures of hydrated alite and synthesized hydrous calcium sulfoaluminates. The absorptions of  $\text{SO}_4^{2-}$  ion in hydrated cements cured for 90 and 365 days correspond to less than 2.9 wt. % of trisulfate, or to less than 4.8 wt % of monosulfate, by comparisons with data from Fig. 5, disagreeing with the calculated contents. These results indicate that the sulfoaluminates in cement paste change gradually to other  $\text{SO}_3$ -bearing phases during the curing period of 1 to 365 days or more. Many other investigators, and the author,<sup>14, 15</sup> showed that hydrous calcium trisulfoaluminate produced immediately after the addition of water to cement should change to monosulfate, and then to the solid solution of monosulfate and calcium aluminate hydrate during the period of the hydration of the aluminates. A further reaction

**Table 1. Chemical compositions of cements and clinker.**

No.	Kind	Chemical Compositions (%)										Potential C <sub>3</sub> A (%)
		Loss on ignition	Insol. residue	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	
C-1	cement	2.1	0.2	20.0	5.4	2.4	63.9	3.0	2.4	0.17	0.14	10.3
C-2		3.1	0.0	23.9	3.6	0.30	65.9	1.1	1.9	0.06	0.31	9.0
C-3		1.4	0.1	21.4	2.6	6.2	65.2	0.6	1.9	0.24	0.25	0.0
C-4		1.9	0.2	23.1	4.3	0.17	85.8	1.4	2.4	0.55	0.15	11.1
K-1	clinker	1.6	0.0	23.7	4.0	0.16	68.1	1.5	0.3	0.74	0.16	10.3

Note 1. Potential C<sub>3</sub>A are calculated by the formula of  $C_3A = 2.65 Al_2O_3 - 1.69Fe_2O_3$ .

Note 2. C-1, 2 and 3 were distributed by the committee, and C-4 and K-1 were supplied by the authors.

**Figure 1. IR spectra of unhydrated and partially hydrated cement (w/c = 0.65) (KBr).**

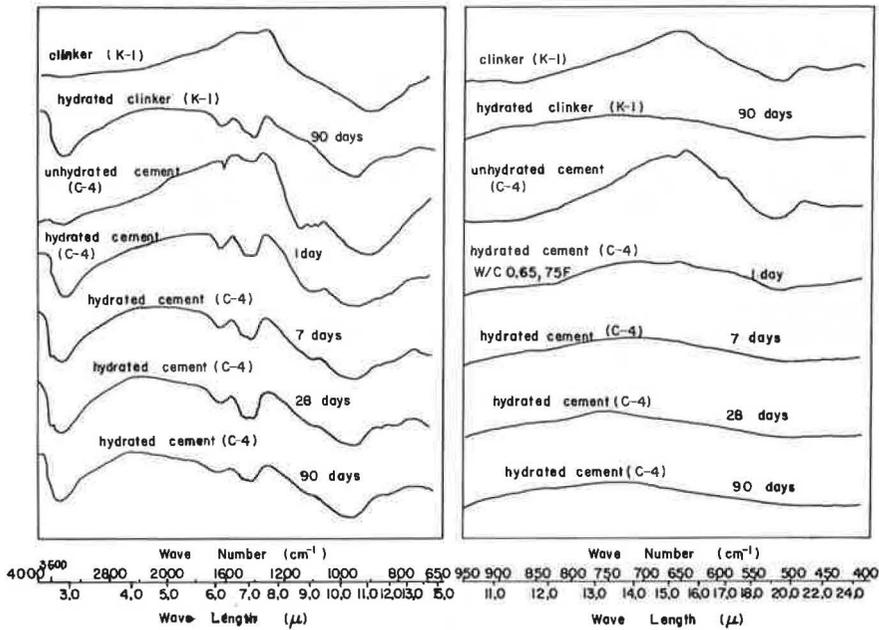


Figure 2. IR spectra of hydrated compounds (KBr).

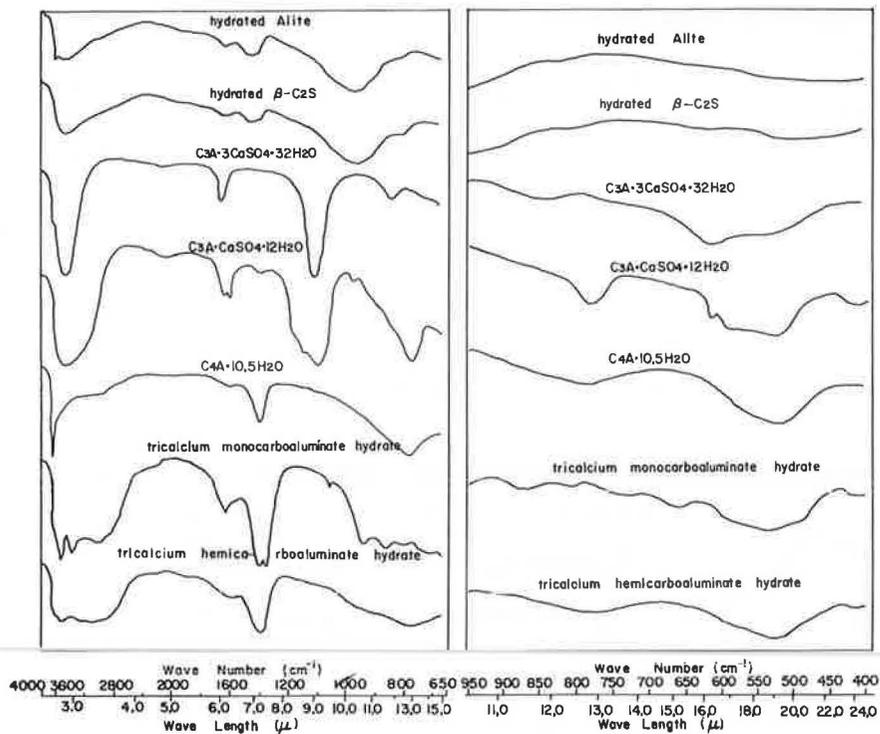


Figure 3. Absorption of SO<sub>4</sub><sup>2-</sup> ion in unhydrated and partially hydrated cement (w/c = 0.65) (KBr).

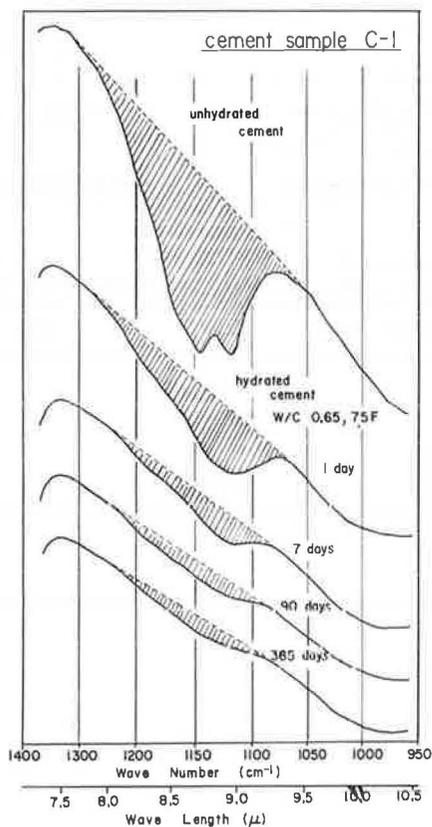


Figure 4. Relation between area of absorption of  $\text{SO}_4^{2-}$  ion in partially hydrated cement and curing period ( $w/c = 0.65$ ) (KBr).

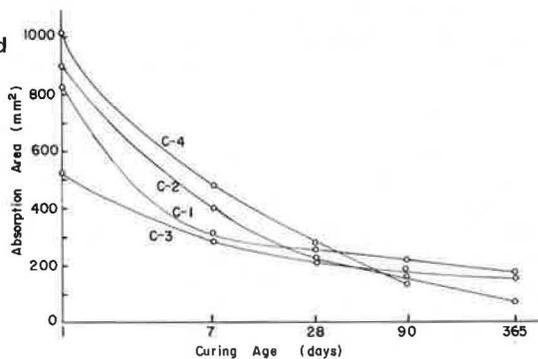
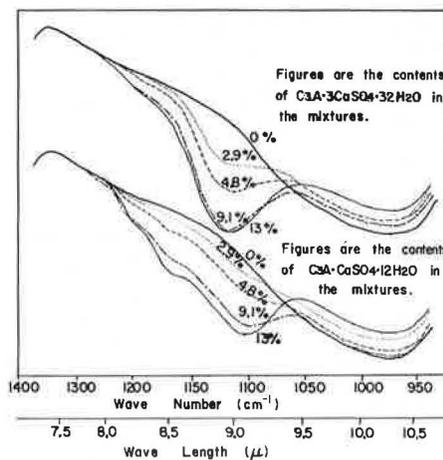


Figure 5. IR spectra of the mixtures of hydrated alite and hydrous calcium sulfoaluminate.



suggested by Kalousek<sup>16</sup> was that the solid solution combines with calcium silicate hydrate to produce a new phase named "x". It is uncertain at the present time to which stage in these reactions the decrease of  $\text{SO}_4^{2-}$  absorption in the IR spectra corresponds.

### Conclusion

The IR spectra of hydrated cements are almost the same as that of hydrated alite, especially at later ages, except for the absorption due to  $\text{SO}_4^{2-}$  ion vibrations in the hydrous calcium sulfoaluminates. The absorption of  $\text{SO}_4^{2-}$  ion in hydrated cement, however, decreases with increasing hydration of cement, and is small at 365 days, suggesting changes in the sulfoaluminates. The IR spectra of the pure phase of ettringite ( $\text{C}_4\text{AH}_{10.5}$ ) suggests that it contains two kinds of water of crystallization. IR of  $\text{C}_3\text{A}\cdot 10.5\text{H}_2\text{O}$  suggests that most of its water of crystallization is in the form of the  $\text{OH}^-$  ion, without hydrogen bonding.

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