

# CIRCULAR

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## Evaluation of Methods of Identifying Phases of Cement Paste

Subject area  
32 cement and concrete

### PREFACE

Of fundamental importance in work on materials are reliable analytical methods for the qualitative and quantitative determination of the phases present. This problem is especially difficult with hardened portland cement paste, because it is made up of many phases most of which are poorly crystalline, finely-divided, and of somewhat variable composition. The purpose of this study by a subcommittee of Committee A2E06 was to examine the utility -- strengths and weaknesses -- of three commonly used analytical methods: X-ray diffraction, differential thermal analysis, and infrared spectroscopy in the analysis of hardened cement paste.

The study was started in 1963 and completed in 1966. The first chairman of the subcommittee was G. L. Kalousek, who was succeeded in 1970 by W. L. Dolch. For various reasons, some good, the results of the study are only now being published. Naturally, some work on the topics to which this study was addressed has taken place in the interval. But the results of this study are still germane and important, and will be a useful addition to the literature, supplemented by the ensuing research.

The committee wishes to record its thanks to Dr. Kalousek for his inspired conduct of the subcommittee's investigation. His planning, coordination, and review of the study contributed greatly to its success.

W. L. Dolch

### INTRODUCTION

#### Purpose

Attempts to relate the properties of concrete to the chemistry of cement have moved ahead slowly. Hydrated cement is a complex material. Up to about 30 different phases have been reported as potential constituents. An obvious approach to accelerate progress is through improvements in research instrumentation and techniques. A second requirement is ready availability of pure hydrates as reference standards for research purposes. A third need is a convenient method for estimating amounts of unhydrated cement phases, especially alite and belite. So it was decided to undertake a cooperative research program to evaluate the potential of several standard analytical techniques to determine the phase composition of partially hydrated portland cement pastes.

It was evident that attainment of this objective would require a sizable program and cooperation of many qualified investigators. A considerable amount of interest in such an undertaking was expressed by the membership of Committee A2E06. A cooperative program was started that involved tests on 37 samples, using X-ray diffraction, differential thermal analysis, and infrared absorption. Eleven laboratories in three countries participated. The participants had complete freedom in following their own procedures,

so in this sense, the program was actually a cooperative research effort, rather than a statistical test series.

### Participants

The participants in the program are listed below. They performed and supervised analyses and/or prepared sample materials. Their efforts, and the cooperation of their companies, are gratefully acknowledged:

R. L. Angstadt, Horace Berman, Kimbe Chujo, K. T. Greene, Nathan Greening, G. L. Kalousek, David L. Kantro, Alexander Klein, J. E. Kopanda, Katharine Mather, P. K. Mehta, H. G. Midgley, R. C. Mielenz, Alice Moore, Yuichi Suzakawa, K. Watanabe, and Taro Yamaguchi.

### Samples

The seven individual hydrates were as follows: Ettringite ( $C_6\bar{A}\bar{S}_3H_{32}$ )\*, tetracalcium aluminate monosulfate - 12 - hydrate ( $C_4\bar{A}\bar{S}H_{12}$ ), tetracalcium aluminate carbonate - 11 - hydrate ( $C_4\bar{A}\bar{C}H_{11}$ ), tetracalcium aluminate hemicarbonatate - 12 - hydrate ( $C_4\bar{A}\bar{C}_{0.5}H_{12}$ ), tetracalcium aluminate hydrate ( $C_4\bar{A}H_9$  in contact with water,  $C_4\bar{A}H_{13}$  at ambient humidities, but present sample was deliberately dehydrated to  $C_4\bar{A}H_{10.5}$  in an attempt to stabilize it against decomposition to  $C_3\bar{A}H_6$ ), alite (impure  $C_3\bar{S}$ ) hydrated for about 5.4 years at 70F, and belite (beta  $C_2\bar{S}$ ) similarly hydrated. The properties of the compounds are listed in the report of the subcommittee on nomenclature of Committee A2E06<sup>1</sup>. The analyses of the first five substances listed above are in Table 1.

The 30 partially hydrated cement pastes were prepared with three portland cements, using water to cement (w/c) ratios of 0.35 and 0.65 by weight and curing times of 1, 7, 28, 90, and 365 days at 75° F. The analyses and computed compound compositions of the cements are given in Table 2. Cement 1 can be regarded as representative of the average composition of Type I portland cements. Cement 2 is a white cement. Cement 3 is designated usually as a zero  $C_3\bar{A}$ , Type I, selected for its high  $C_4\bar{A}F$  content. Cement 4 and the clinker from which it was made (No. 5) were used by one participant in infrared absorption tests.

### Preparation of Cement Paste Samples

The cement and water were mixed in a stoppered flask for 3 minutes, and the resulting slurry was put into 10 polyethylene vials. The tightly stoppered vials were stored in a desiccator. At the end of each curing period two specimens were removed, and the top and bottom 1-inch portions were cut off and discarded. The remainder, about 100 g, was rapidly crushed to approximately -20 sieve size. The resulting powder was dispersed in about 5 volumes of dry acetone to 1 part bulk sample in a sintered-glass filtering crucible. After a 3-minute soaking period the suspension was subjected to suction. During filtration, the sample was continually and firmly compacted with a 3/4-inch-diameter glass rod in order to remove a maximum amount of the liquid and prevent passage of air through the sample. Immediately after removal of the liquid, the sample was transferred to a glass vial, which was stoppered and set aside. The vials of a group of samples were then unstoppered and placed in a desiccator connected to a laboratory vacuum pump. The samples were degassed for 24 hours. The hydrated alite and belite were similarly processed.

The above method of drying was based on results of preliminary experiments involving samples of cement pastes cured for 1 to 28 days in 10-to-100 g lots and degassed for 6 to 24 hours. Differential thermal analysis (DTA) was applied to detect "free" water, which was indicated by an endotherm at about 110-120° C superimposed on the endotherm of tobermorite gel. The 1-day sample in a 10-g lot was considered dried properly after 6 hours of degassing, and further drying to 24 hours had no significant effect on the size of the endotherms of C-S-H gel or ettringite. A 100-g sample cured for 20 days required nearly 18 hours of degassing to remove the free water, but underwent no further change during an additional 6 hours of degassing. On the basis of these observations, a 24-hour period of degassing was used. Obviously, a phase such as  $C_4\bar{A}H_9$

\*The usual abbreviations of cement chemistry are used: C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O,  $\bar{S}$  = SO<sub>3</sub>,  $\bar{C}$  = CO<sub>2</sub>, N = Na<sub>2</sub>O, K = K<sub>2</sub>O

1. "Guide to Compounds of Interest in Cement and Concrete Research," Highway Res. Board, Spec. Rept. 127 (1972).

Table 1. Compositions of pure phases.

	Ettringite	Monosulfate	Monocarbo- aluminate	Hemicarbo- aluminate	$C_4AH_{10.5}$
No.	41	39	38	37	40
CaO, %	27.16	36.13	39.83	39.71	43.35
Al <sub>2</sub> O <sub>3</sub> , %	8.21	16.27	17.58	17.68	19.67
SO <sub>3</sub> , %	19.25	12.72	-	-	-
CO <sub>2</sub> , %	0.04	0.00 <sub>5</sub>	7.59	3.76	0.57
H <sub>2</sub> O, %	45.54	34.77	-	38.36(a)	36.41(a)
Ignition Loss, %	-	-	42.19	42.12	36.98

(a) difference

The Sulfoaluminate samples had the following compositions:

	Weight, percent	Mole, percent
Monosulfate (No. 39)	99.50	96.3
Ca(OH) <sub>2</sub>	0.45	3.7
Carbonate	0.00	-
Ettringite (No. 41)	99.34	95.5
Ca(OH) <sub>2</sub>	0.52	4.0
CaSO <sub>4</sub> · $\frac{1}{2}$ H <sub>2</sub> O	0.14	0.5
Carbonate	0.00	-

Table 2. Oxide and computed phase compositions of cements 1 to 4 and clinker, No. 5.

	Cement No.				
	1	2	3	4	5
<u>OXIDES,</u> <u>percent</u>					
SiO <sub>2</sub>	20.2	23.7	21.5	23.1	23.7
Al <sub>2</sub> O <sub>3</sub>	5.4	3.4	3.0	4.3	4.0
Fe <sub>2</sub> O <sub>3</sub>	2.5	0.5	6.0	0.17	0.16
CaO	63.7	66.2	65.2	65.8	68.1
MgO	3.1	1.3	0.8	1.4	1.5
MnO	0.51	0.01	0.04	-	-
SO <sub>3</sub>	2.5	2.0	2.0	2.4	0.3
K <sub>2</sub> O	0.13	0.31	0.22	0.55	0.74
Na <sub>2</sub> O	0.14	0.04	0.15	0.15	0.16
Loss on ignition	1.8	2.6	1.9	1.9	1.6
<u>PHASES (Computed),</u> <u>percent</u>					
C <sub>3</sub> S	58.9	60.0	65.6	56.3	69.2
C <sub>2</sub> S	13.5	22.8	12.1	23.8	15.7
C <sub>3</sub> A	10.0	8.2	0.0	11.1	10.3
Ferrite	7.7	1.7	16.6	0.5	0.5
CaSO <sub>4</sub>	4.2	3.4	3.4	4.1	0.5

would not survive this type of drying, and would be altered to  $C_4AH_{13}$ . Dry organic liquids such as ethyl alcohol, acetone, etc., when used repeatedly in washing a given sample may dehydrate some of the hydrates. For this reason only one washing with acetone was used. This procedure may not be the best, but so far as results of preliminary tests described above show, the samples did not appear either to be underdried or overdried.

A second problem is that of carbonation. Facilities with  $CO_2$ -free air were not available. The extent of carbonation was minimized by the rapid handling of large samples (about 100g) during exposure to air. DTA results on the pastes, compared to DTA results on blends of known amounts of a  $CO_2$ -free cement paste and calcite, indicated that two of the thirty samples contained 0.4-0.5 percent  $CO_2$ , three contained 0.2 percent or slightly less, and the remainder 0.1 percent or less. About half of the samples showed no calcite endotherm when tested at 100-percent sensitivity; the threshold content for detection was 0.05 percent  $CO_2$  as calcite at this sensitivity.

The samples in polyethylene vials were stored in a desiccator over ascarite. Samples in polyethylene vials deliberately exposed to air for 1 year were found carbonated to the extent of 0.2 to 1.0 percent  $CO_2$ .

#### THE QUANTITATIVE DETERMINATION OF ALITE AND BELITE RESIDUES IN PARTLY HYDRATED CEMENT PASTES

David L. Kantro, Portland Cement Association

The work to be described in this report is a part of the cooperative program on Evaluation of Methods of Identifying Phases of Cement Pastes, sponsored by the Transportation Research Board Committee A2E06. Although the present results pertain to a method of analysis, rather than identification, the data were obtained by an X-ray method, and consequently lie within the scope of the program.

The method used has been reported previously (1) and has been applied to partly-hydrated pastes by Copeland (2).

The present results include alite and belite contents as functions of age for pastes of three different cements used in the A2E06 program. The study was limited to these two major contributors to cementitious properties.

#### Experimental

The three cements used in this investigation, and their oxide compositions, were provided by G. L. Kalousek. The oxide compositions of these cements are given in Table 1. One of the three is a normal cement, one is a white cement, and one is a nominal zero-percent- $C_3A$  cement. The first two were of the same brands, but not from the same lots, as the samples used by other investigators on the program. The oxide compositions in these two cases differed slightly, but not significantly, from the oxide compositions of the cements used elsewhere. The third, the nominal zero-percent- $C_3A$  cement, was from the same lot as the samples used by other investigators in the program.

Paste series from each cement were made at two water/cement ratios, 0.35 and 0.65. Samples of each series were hydrated for periods of 1, 3, 7, 14, 28 and 90 days. The ignition loss of each paste, and the alite and the belite contents were determined.

The pastes were mixed in an evacuated 500 ml brass cylinder which was shaken for 6 minutes in a modified paint-can shaker. The mixes were cast in 1-1/4-in. i.d. polyethylene test tubes, which were then stored at 23.5°C. Each sample was removed from its test tube at the end of its prescribed hydration period. The top and bottom 1/2-in. of the sample were discarded, and the remainder was placed in a vacuum drying apparatus (3). After two or three days of drying, the sample was removed, ground -80 mesh in a controlled atmosphere glove box, and returned to the drying apparatus. Each sample was dried approximately 4 weeks after grinding.

The dried samples were used for X-ray and loss on ignition (1050°C) determinations. Mixtures with silicon for the X-ray work were prepared with a vibratory ball mill, as described by Copeland and Bragg (4).

The X-ray determinations were made using a North American Philips Geiger counter diffractometer and also with a diffractometer incorporating a proportional counter and pulse height analyzer. The radiation was  $CuK\alpha$  Ni-filtered. Scanning speed was 1/8° 2 $\theta$  per minute.

#### The X-ray Method

Of the two published alternative methods (1), the procedure involving oxide composition

data cannot be used because the oxide composition of the clinker residue is not known. Hence, the method utilizing only X-ray data must be employed.

Although beyond the scope of the present study, it should be pointed out that the determination of tricalcium aluminate and ferrite phase residues in partly hydrated portland cement pastes cannot be made directly on the paste. X-ray lines from the hydration products interfere with the lines to be measured. In order for such an analysis to be made, the paste sample must first be freed of calcium hydroxide, as Copeland has done using a selective extraction procedure (2). It would be of greater advantage if the extraction procedure removed the calcium silicate hydrate as well.

When only alite and belite residues are to be determined, as in the present investigation, the paste samples need not be extracted. There is a small overlap of the calcium hydroxide line at  $51.6^\circ 2\theta$  with the alite-belite line at  $52.8^\circ 2\theta$ . This overlap can be corrected geometrically before the  $52.8^\circ 2\theta$  is measured.

Silicon was used as an internal standard. In pastes, however, the silicon line at  $28.4^\circ 2\theta$  used in cement analysis, is interfered with by calcium hydroxide and calcium silicate hydrate gel lines, and cannot be used. The silicon line at  $88^\circ 2\theta$  was employed instead (2).

The equations used for alite-belite determination in cements must be modified for the change in silicon line. The intensity of the  $28.4^\circ 2\theta$  silicon line is therefore calculated from the intensity of the  $88^\circ 2\theta$  line, using the intensity ratio of these lines as determined from pure silicon samples and from cement-silicon mixtures. The value obtained in the present investigation for  $I_{88}/I_{28.4}$  is 0.15. Swanson and Fuyat (5) report a value of 0.17. Apparently each investigator employing this method should determine the ratio  $I_{88}/I_{28.4}$  with the same equipment as used for the analysis.

The quantity of silicon used in the present application was 15 percent by weight of the paste. Previously, for cement analysis, 10 percent had been used. The amount was increased for the present purposes in order to obtain a more intense  $88^\circ (2\theta)$  diffraction line.

The quantities obtained by the X-ray method are the weight ratios of alite to silicon,  $x_1$ , and belite to silicon,  $x_2$ . The equations, given below, relating the intensity ratios to these quantities, have been derived previously (1).

$$\frac{x_2}{x_1 + x_2} = w_2 = \frac{-(B_1 + B_2 R_3)}{2(A_1 + A_2 R_3)} + \frac{\sqrt{(B_1 + B_2 R_3)^2 - 4(A_1 + A_2 R_3)(C_1 + C_2 R_3)}}{2(A_1 + A_2 R_3)} \quad (1)$$

$$x_1 + x_2 = - \frac{R_1}{A_2 w_2^2 + B_1 w_2 + C_1} \quad (2)$$

where  $R_1$  is the intensity ratio of the  $51.8^\circ 2\theta$  line,  $I_{51.8}$ , to the  $28.4^\circ 2\theta$  silicon line,  $I_{28.4}$ , or when the  $88^\circ 2\theta$  line is used,  $0.15 I_{51.8}/I_{88}$ ;  $R_3$  is the intensity ratio  $I_{51.8}/I_{41}$ . The quantities  $A_1$ ,  $B_1$ ,  $C_1$ ,  $A_2$ ,  $B_2$  and  $C_2$  are constants whose values have been previously determined (1).

The value of  $w_2$  is calculated from equation (1) and is then used in the calculation of  $x_1 + x_2$  from equation (2). The quantities  $x_1$  and  $x_2$  can be easily obtained from  $w_2$  and  $x_1 + x_2$ . The alite and belite contents are finally obtained as the products  $P_0 x_1$  and  $P_0 x_2$ , where  $P_0$  is the quantity of silicon in grams per gram ignited weight of paste. The quantity  $P_0$  is obtained from the original mixture composition and the ignition loss (at  $1050^\circ\text{C}$ ) of the original paste.

## Results and Discussion

The phase compositions of the three cements were determined by the X-ray method (1); the results are given in Table 1.

The results of the paste studies are given in Table 2. The alite and belite contents of the original cements are included in the table (0 days hydration) for comparison.

The experimental error in the reported alite values varies from  $\pm 3$  percent (absolute) for the highest values to  $\pm 1$  percent for the lowest. The experimental error in the belite varies from  $\pm 8$  percent in the highest values to  $\pm 4$  percent in the lowest values. The belite error is larger than the alite error, because the  $51.2^\circ 2\theta$  line used in the determination is primarily an alite line and contains only a weak belite component. The experimental error can be reduced by any means that will increase the number of X-ray counts measured in the determination, such as more scans, or slower scanning, or by extraction of the calcium hydroxide from the paste, which leaves a

**Table 1. Compositions of the original cements.**

Cement	Normal	White	Nominal O% - C <sub>3</sub> A
Oxides, percent			
SiO <sub>2</sub>	20.0	24.8	21.5
Al <sub>2</sub> O <sub>3</sub>	5.28	3.28	3.02
Fe <sub>2</sub> O <sub>3</sub>	2.50	0.33	6.04
CaO	63.9	66.2	65.2
MgO	2.9	1.4	0.8
MnO	0.47	0.02	0.04
SO <sub>3</sub>	2.4	2.4	2.0
Alkali	0.20	0.16	0.37
Fineness, cm <sup>2</sup> /g Blaine	3130	2770	3020
Compounds (XR Method)			
Ferrite, molar A/F	1.02	1.36	0.43
percent	9.2	1.2	13.9
C <sub>3</sub> A, percent	5.7	5.1	1.4
Alite, percent	57.8	50.8	67.2
Belite, percent	19.5	40.0	13.7

**Table 2. Ignition losses and alite and belite residues in partly hydrated cement pastes.**

Cement Paste Age days	Normal			White			Nominal O% - C <sub>3</sub> A		
	Ign. Loss % ign.wt.	Alite % ign.wt.	Belite % ign.wt.	Ign. Loss % ign.wt.	Alite % ign.wt.	Belite % ign.wt.	Ign. Loss % ign.wt.	Alite % ign.wt.	Belite % ign.wt.
	0.35 w/c pastes								
0		57.8	19.5		50.8	40.0		67.2	13.7
1	6.7	37.5	16.2	5.3	32.0	35.3	6.9	41.6	11.2
3	10.3	28.5	18.1	9.0	21.1	32.8	10.5	25.0	9.7
7	12.7	18.6	13.7	11.5	12.3	29.1	12.2	20.7	8.8
14	14.6	15.8	12.1	13.3	7.8	29.3	13.1	16.2	8.1
28	15.8	11.8	7.1	14.3	8.8	21.4	14.3	12.9	7.3
90	17.7	9.2	2.8	15.8	6.2	15.4	15.4	9.4	5.5
	0.65 w/c pastes								
0		57.8	19.5		50.8	40.0		67.2	13.7
1	7.0	37.9	17.0	6.2	29.7	35.2	7.7	34.1	11.0
3	11.1	23.4	12.2	10.2	15.1	31.2	11.1	22.4	6.3
7	14.3	15.7	12.0	12.1	9.6	27.9	12.9	17.0	7.6
14	17.0	11.4	8.4	13.2	6.9	25.9	14.2	12.6	6.4
28	18.3	7.1	6.9	15.0	5.1	24.0	15.2	3.2	11.2
90	20.7	3.4	1.2	17.2	7.8	7.9	18.3	4.0	4.4

Figure 1. Degree of hydration versus time, alite and belite phases, normal portland cement.

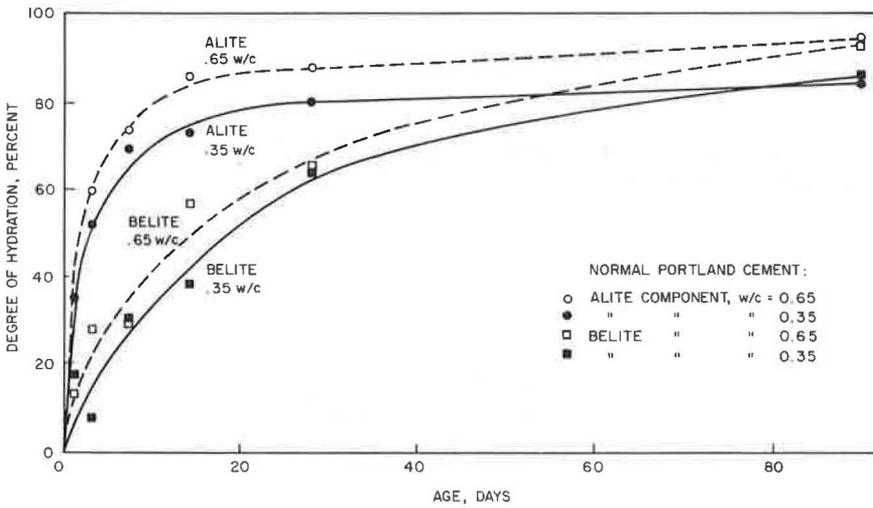


Figure 2. Degree of hydration versus time, alite and belite phases, white portland cement.

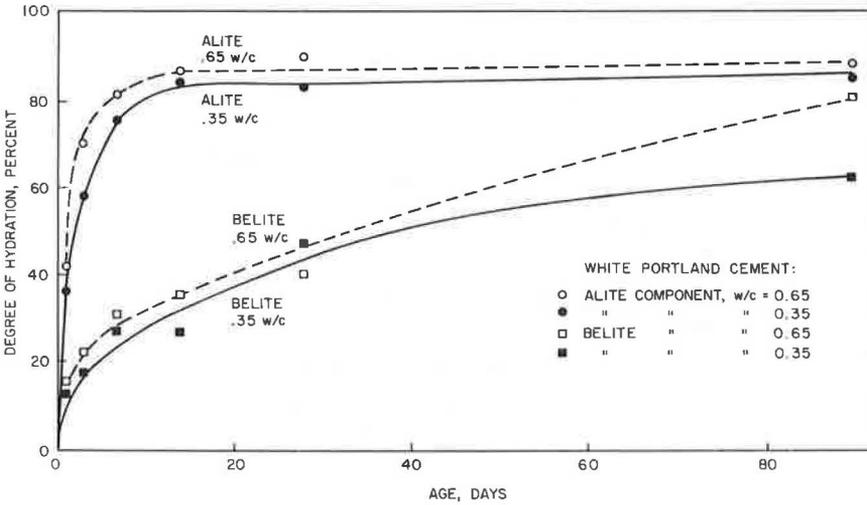


Figure 3. Degree of hydration versus time, alite and belite phases, zero percent C<sub>3</sub>A.

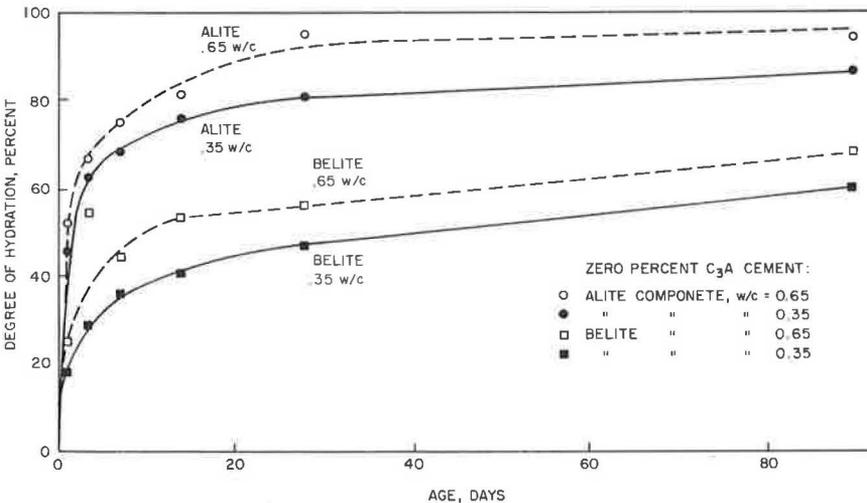


Figure 4. Degree of hydration versus time, alite phase, three different cements.

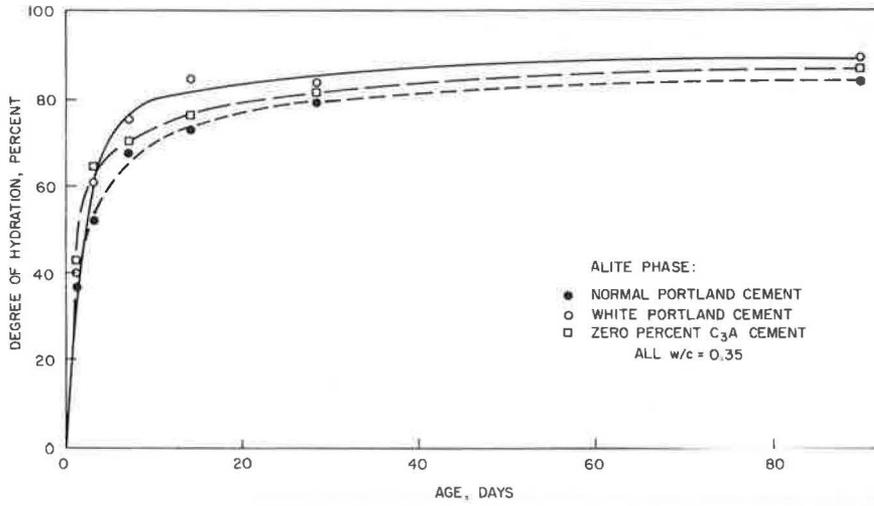
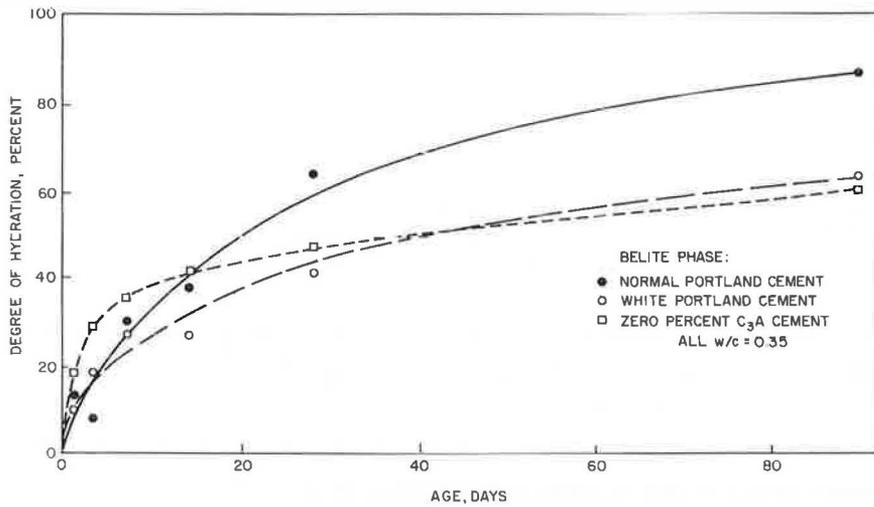


Figure 5. Degree of hydration versus time, belite phase, three different cements.



residue enriched with respect to the unhydrated components.

The degree of hydration of alite and belite in the various pastes, as a percentage of the quantity originally present, can be obtained from the data in Table 2. The values are plotted as functions of time in Figs. 1, 2, and 3.

The effect of water/cement ratio on the degree of hydration can be seen in Figs. 1, 2, and 3. For all three cements, at any given paste age, the degree of hydration is lower at the lower water/cement ratio.

The slower hydration of belite, relative to alite, is shown by the curves. This effect, as well as the water/cement ratio effect, is clear, in spite of the relatively large experimental error in the belite determination.

For the three cements used in the present investigation the alite contents vary from 50 to 67 percent and the belite contents vary from 13 to 40 percent in the unhydrated materials. One cement has practically no  $C_3A$  while another has no ferrite phase. The alite and belite hydration data have been compared for any gross differences between cements. The data for the degree of hydration of alite for the three 0.35 w/c series are plotted as functions of time in Fig. 4. The differences among the three curves are small. The white cement curve is slightly higher, although the white cement was of slightly lower fineness (Table I). Whether the higher percentage of alite hydration is related to the absence of iron in the system or is the result of the lower initial content cannot be determined from these data.

The results for the degree of hydration of belite for the three 0.35 w/c series are plotted as functions of time in Fig. 5. At relatively early ages, up to 14 days, there is some correlation between degree of hydration at a given time and initial belite content. At later ages, a significantly greater fraction of the belite has hydrated in the normal portland cement case than in the other two. At the higher w/c ratio, however, both the normal and white cement belite have hydrated to a greater extent than the belite in the zero- $C_3A$  cement.

The results presented here illustrate an application of X-ray diffraction to the study of hydrated pastes. The method has several useful functions. It is being used as a research tool to determine the influence of cement composition and other variables on the rates of hydration of alite and belite. The X-ray method may also prove useful in explaining unusual hydration characteristics when encountered.

### Summary

The alite and belite contents of the clinker residue of partly hydrated cement pastes can be obtained by X-ray quantitative analysis.

The X-ray method used is essentially the same as that for unhydrated cements.

The results of determinations on pastes from three different portland cements demonstrates the increase in hydration both of alite and belite at any given time with increase in the water/cement ratio.

### References

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### EXAMINATION OF CEMENT PASTES, HYDRATED PHASES, AND SYNTHETIC PRODUCTS BY X-RAY DIFFRACTION

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### Introduction

One of the techniques used to identify hydration products in cement pastes, hydrated phases, and synthetic products was X-ray diffraction. X-ray diffraction has been

extensively and successfully used to study materials of these types by Flint, McMurdie, and Wells,<sup>1</sup> Taylor,<sup>2, 4</sup> Heller and Taylor,<sup>3</sup> Turriziani and colleagues,<sup>5,6,7</sup> Kalousek,<sup>8</sup> Midgley,<sup>9</sup> Kantro, Copeland, and Anderson,<sup>10</sup> and many others.

The work reported here is the first cooperative investigation by X-ray diffraction of pastes and synthesized hydrates of which we are aware. All of the participants performed a service to the community of cement and concrete research.

### Participants

The participating laboratories are listed below. They are identified in subsequent tables by numbers that do not correspond to the listed order.

- a. Building Research Station, Garton, Watford, Herts., UK
- b. Ideal Cement Company, Fort Collins, Colo., USA
- c. Portland Cement Association Research and Development Laboratories, Skokie, Ill., USA
- d. Ube Kosan Company, Ltd., Central Research Laboratory, 1978-6 Ohaza Kogushi, Uke-Shi, Yamaguchi-Ken, Japan
- e. Universal Atlas Cement Division, Buffington, Ind., USA
- f. Engineering Materials Laboratory, University of California, Berkeley, Calif., USA
- g. Waterways Experiment Station, Concrete Division, Vicksburg, Miss., USA

### Approach

Participants were asked to make their examinations and report their data as they usually did, and if they wished to do so, to modify their procedures. As a consequence of these instructions, procedures differed widely from laboratory to laboratory. In some cases procedures were modified within a laboratory in the course of the program. While the absence of prescribed procedures led to differences in results, the opportunity to compare results obtained by following different procedures with different instruments was valuable.

### Samples - Cement Pastes

The Research Laboratories of the Universal Atlas Cement Division prepared and distributed cement pastes (Table 1), which were examined by six of the participants. Pastes were prepared at water-cement ratios of 0.35 and 0.65 with three cements: a type I cement of average composition, a white cement, and a zero C<sub>3</sub>A cement. The pastes were cured at 75 F for 1, 7, 28, 90, and 365 days. Twenty-eight of the 30 paste samples contained 0.0 to 0.2 percent CO<sub>2</sub>; the other two had 0.4 to 0.5 percent CO<sub>2</sub>. Hydration was terminated at the selected age by crushing the paste to pass a No. 20 sieve, washing the crushed sample in acetone, and then immediately subjecting it to suction filtration. The sample was then dried in vacuum for 24 hours at 40-50  $\mu$ m Hg.

The seventh participant later prepared pastes at the same two water-cement ratios, and cured them for 1, 3, 7, 14, 28, and 92 days. Each paste was examined as a wet lapped slice and as a dried powder. The results obtained were similar to those obtained by examining the pastes originally distributed.

### Samples - Hydrates and Synthetic Products

Samples of hydrates of alite and  $\beta$ -C<sub>2</sub>S, and of synthetic products (Table 1) were examined by most of the participants (Table 2). The preparation of the calcium aluminate monosulfate used in this program has been described.<sup>11</sup>

### Instrumentation

The instruments used by the cooperating laboratories are identified in Table 3. Five of the diffractometers were standard models, but the sixth was equipped with a fine-focus X-ray tube, curved-crystal monochromator, and a Geiger-counter detector. The seventh laboratory used a focusing camera (of the Guinier type) with monochromatic copper radiation, because they had found it better able to detect weak lines, and thus to detect small quantities, than their diffractometer. Operating conditions reported are shown in Tables 4a and 4b.

Table 1. Samples.

Comment	W/C	Sample Numbers of Pastes				
		Curing Period, Days				
		1	7	28	90	365
No. 1 (Type I)	0.35	1	2	5	13	25
No. 1 (Type I)	0.65	3	4	6	14	26
No. 2 (White)	0.35	7	8	11	15	27
No. 2 (White)	0.65	9	10	12	16	28
No. 3 (Zero C <sub>3</sub> A)	0.35	17	18	21	23	29
No. 3 (Zero C <sub>3</sub> A)	0.65	19	20	22	24	30

Laboratories 1 through 4, and 6, examined all 30 samples.  
Laboratory 5 examined samples 7 through 30.

## Hydrated Phases and Compounds

Sample No.	Description	Source
35	Hydrated alite Hydrated 5.3 years	PCA
36	Hydrated $\beta$ -C <sub>2</sub> S Hydrated 5.3 years	PCA
37	Tetracalcium aluminat hemicarboaluminate-12-hydrate	PCA
38	Tetracalcium aluminat carbonate-11-hydrate	PCA
39	Tetracalcium aluminat monosulfate-12-hydrate	NBS
40	Tetracalcium aluminat-10.5-hydrate	PCA
41	Ettringite	NBS
-	Ettringite	PCA

Table 2. Hydrated phases examined by six laboratories.

Sample No.	Description	Laboratory Number					
		1	2	3	4	5	6
35	Hydrated alite*	x	x	x	-	x	x
36	Hydrated $\beta$ -C <sub>2</sub> S*	x	x	x	-	x	x
37	Tricalcium hemicarboaluminate*	x	x	x	x	x	x
38	Tricalcium monocarboaluminate*	x	x	x	x	x	x
39	Calcium monosulfaluminate**	x	x	x	x	-	x
40	C <sub>4</sub> AH <sub>10.5</sub> *	x	x	x	-	x	x
41	Ettringite**	x	x	x	-	x	x
-	Monosulfate (0.75 SO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> )*	-	-	x	-	-	-
-	Ettringite*	-	-	x	-	-	-

\* Prepared by the Portland Cement Association Research and Development Laboratories.

\*\* Prepared by the National Bureau of Standards.

Table 3. Instrumentation.

	Laboratory						
	1	2	3	4	5	6	7*
Diffractometer							
General Electric	-	x	x	-	-	-	-
Norelco	x	-	-	x	-	-	x
Rigaki Denki	-	-	-	-	x	-	-
Guinier Camera	-	-	-	-	-	x	-
Monochromator	-	-	-	-	-	x	x**
Radiation	Cu	Cu	Cu	Cu	Cu	CuK $\alpha$	CuK $\alpha$
Filter	Nickel	Nickel	Nickel 0.0007 in.	Nickel 0.0007 in.	Nickel	-	-
Detector							
Film	-	-	-	-	-	x	-
Proportional Counter	x	-	x	-	-	-	-
Scintillation Counter	-	-	-	x	x	-	-
Geiger Counter	-	-	-	-	-	-	x

\* One examination made using a high-intensity X-ray tube, nickel filter, pulse height analysis, and a proportional counter as a detector.

\*\* Curved crystal monochromator with fine focus X-ray tube and geiger counter detector.

### Examination of Pastes

X-ray diffraction was one of the methods used to identify and characterize hydration products in pastes. The specific intentions in the X-ray portion of the program included determining the sequence of hydration products developed in the three cements and the number and kinds of products detected by different laboratories with different instrumentation.

The hydrated alite and belite and the synthetic products offered the participants the opportunity of examining carefully prepared samples of substances that are present or may be present in pastes and concretes. It also presented an opportunity for comparing effects of conditions during storage and examination on some of the substances.

### Results

As previously stated, no instructions on procedures were included, with the result that in some of the participating laboratories the samples were subjected to routine examination, while in others procedures were adjusted carefully to the samples to maximize the information obtained. The previous experience of the operators in examining hydrated cement pastes ranged from nil to several years; the expertise of the operators also ranged widely. Because of the variations in approach, experience and expertise, the detail obtained and reported also differed considerably from laboratory to laboratory. All these variations should be borne in mind in studying the tables of constituents identified in the cement pastes.

One of the laboratories ranked the constituents reported as follows:

- C = Compound certainly present (at least three lines detected)
- P = Compound probably present (at least two strong lines detected; other overlapped)
- D = Presence of compound can be doubted (one or two lines just detectable; others overlapped)
- U = Undetected

Two listed the interplanar spacings which each regarded as diagnostic of the constituent identified.

	<u>Interplanar Spacings, d, m x 10<sup>-10</sup></u>	
	<u>Laboratory 3</u>	<u>Laboratory 6</u>
Ettringite	9.8	9.8
C <sub>4</sub> ASH <sub>12</sub>	8.9	8.9
C <sub>4</sub> AC <sub>0.5</sub> H <sub>12</sub>	8.2	8.2
C-A hydrate	-	7.9
C <sub>4</sub> ACH <sub>11</sub>	7.7	7.7
Calcium hydroxide	4.90, 2.63	4.9
Hydrogarnet	5.06, 2.54	2.54
C-S-H gel	3.03, 1.82	3.04, 2.98
Alite	2.97, 1.76	2.79
Belite	2.88*	2.88
C <sub>3</sub> A	2.69	2.69
Aluminoferrite SS	7.3, 2.65	7.3, 2.66
MgO	2.10	2.10
Calcite	**	2.29

\* Line interfered with by C<sub>4</sub>ASH<sub>12</sub>

\*\* With cement No. 1, 2.10, 2.28; with cement No. 2, 3.88, 2.28, 2.10; with cement No. 3, 3.03, 2.28, 2.10.

Table 5, Characteristic Spacings of Constituents of Portland Cement Pastes, is a modified compilation to show useful spacings and overlaps and interferences.

The compositions of the pastes examined in the program are shown in Tables 6 through 11 in terms of the constituents reported by the participating laboratories as present at each age of the pastes. Partial X-ray diffraction charts are shown in Figs. 1 through 6.

**Table 4a. Operating conditions for examination of cement pastes.**

	Laboratory 1	Laboratory 2	Laboratory 3
KV of X-ray tube	35	50	50 <sup>(a)</sup>
ma of X-ray tube	15	16	16 <sup>(a)</sup>
Apparent watts <sup>(b)</sup>	525	800	800 <sup>(a)</sup>
Detector	Proportional counter	Proportional counter	Proportional counter
Scanning speed, deg/min	0.25	2	0.2
Slits	Divergence: 1 deg Scatter: 1 deg Receiving 0.003 in. <sup>(c)</sup>	Beam 1 deg Medium Resolution Soller Medium Resolution Detector: 0.2 deg	7-20 2θ 1 deg 3 deg 0.2 deg
Chart full scale deflection	Linear, 240 c/s	Linear, 200 c/s	Logarithmic, 4000 c/s <sup>(c)</sup>
Time constant	4 sec	3 sec	30 sec/7.5 sec/2 sec <sup>(d)</sup>
	Scale factor 8 Multiplier 0.6	- -	Not applicable Not applicable
Pulse height selection	No	No	Yes

- (a) Two diffractometers used; the one at 50 KVCP and 21 ma operated at constant potential.  
 (b) (KV × ma) = apparent watts.  
 (c) All pastes of 0.65 w/c were re-examined in the range 7-21 2θ using a linear scale of 1000 c/s, with time constant = 8 sec, except that the Ca(OH)<sub>2</sub> peak at 18 2-θ was also scanned with tc = 4 sec (samples 3, 4, 6, 14, 26; 9, 16; 22, 30) or with tc = 2 sec (samples 26, 9, 10, 12, 16, 19). During this examination, the intensities of all peaks were scaled.  
 (d) In the first, second, and third decades, respectively, of the logarithmic range.

**Table 4b. Operating conditions for examination of cement pastes.**

	Laboratory 4			Laboratory 5			Laboratory 7	
KV of X-ray tube	33 <sup>(a)</sup>	40 <sup>(b)</sup>	40 <sup>(c)</sup>	35	40	40	40	40
ma of X-ray tube	35	30	35	15	18	18	18	35
Apparent watts	1155	1200	1400	525	720	720	720	1400
Detector	Scintillation counter			Scintillation counter			Monochromator with Geiger counter	Proportional counter
Scanning speed	0.25 deg/min	0.5 deg/min	0.5 deg/min	0.5 deg/min	0.125 deg/min	0.125 deg/min	0.125 deg/min	0.125 deg/min
Slits: Divergence	1 deg	1 deg	1 deg	1 deg	1 deg	1 deg <sup>(g)</sup>	1 deg	1 deg
Scatter	1 deg	1 deg	1 deg	1 deg	1 deg	1 deg	1 deg	1 deg
Receiving	0.006 in. -0.006 deg	0.006 in.	0.006 in.	0.2 mm	0.006 in.	0.06 deg	0.006 in.	0.006 in.
Chart full scale deflection	500 c/s	500 c/s	1000 c/s	400 c/s <sup>(d)</sup>	800 c/s <sup>(e)</sup>	1600 c/s <sup>(f)</sup>	100 <sup>(h)</sup> or 200 <sup>(i)</sup> c/s	200 c/s
Time constant	4	2	2	4	4	4	8 sec	8 sec
Pulse height selection	yes	yes	yes	no	no	no	no	yes

- (a) 33 KVp × 35 ma samples 1 through 16  
 (b) 40 KVp × 30 ma samples 17 through 24  
 (c) 40 KVp × 35 ma samples 25 through 30  
 (d) Samples 7 through 20; scale factor 8, multiplier 1  
 (e) Samples 21 through 24  
 (f) Samples 25 through 30; scale factor 32, multiplier 1  
 (g) From 60 to 20 2θ, 1 deg divergence and scatter slits; from 20 to 5 2θ, 0.5 divergence and scatter slits  
 (h) Pastes from 60 to 20 2θ  
 (i) Cements 60 to 20 2θ

**Table 5. Strong lines and interferences in portland cement pastes.**

$d, m \times 10^{-10}$	
9.73 <sup>(1)</sup>	Ettringite I = 100; 9.6 A $C_4A\bar{S}H_{14-15}$ <sup>(2)</sup>
9.0	$C_4A\bar{S}H_{12}$ (0001) <sup>(3)</sup>
8.2	$C_4A\bar{S}H_{10}$ , $C_4A\bar{C}_{0.5}H_{12}$ <sup>(4)</sup> (0001) of both
7.95	$C_4AH_{13}$ <sup>(6)</sup> (0001)
7.77	$C_4A\bar{C}_{0.5}H_9$ <sup>(4)</sup> (0001)
7.62	$C_4A\bar{C}H_{10-11}$ <sup>(4)</sup> (0001)
7.2-7.4	Aluminoferrite solid solutions <sup>(7)</sup> ; 7.2 of $C_4A\bar{C}H_6$ <sup>(4)</sup>
5.94	Alite <sup>(7)</sup>
5.61	Ettringite, I = 81
5.06	Hydrogarnet <sup>(8)</sup> , I = 95
4.90	CH <sup>(1)</sup> ; $C_4A\bar{S}H_{12}$ weak
4.69	Ettringite, I = 36
4.62	$C_4A\bar{C}_{0.5}H_{12}$
4.48	$C_4A\bar{S}H_{12}$ ; $C_4AH_{13}$ weak
4.38	Hydrogarnet, weak but not subject to interference.
4.10	$C_4A\bar{C}_{0.5}H_{12}$ ; $C_4A\bar{S}H_{10}$ (0002)
4.00	$C_4A\bar{S}H_{12}$
3.95	$C_4AH_{13}$ (0002)
3.88	Ettringite; $C_4A\bar{C}_{0.5}H_{10}$ (0002); $C_4A\bar{C}_{0.5}H_{12}$ ; $C_4AH_{13}$ weak; Alite; Calcite weak.
3.78	$C_4A\bar{C}H_{11}$ (0002)
3.66	$C_4A\bar{S}H_{12}$ ; aluminoferrite solid solution 3.63-3.70
3.62	$C_4AH_{13}$ weak
3.48	Ettringite, probably not detected.
3.30	Hydrogarnet, weak but not interfered with in paste
3.112	CH, ordinarily masks 3.10 of Hydrogarnet
3.06	C-S-H <sup>(9)</sup>
3.04	Alite, Belite, 3.035 of calcite <sup>(1)</sup>
2.97	Alite
2.88	$C_4A\bar{S}H_{12}$ , $C_4A\bar{S}H_{10}$ , $C_4A\bar{C}_{0.5}H_{12}$ , $C_4AH_{13}$ ; Belite <sup>(7)</sup> , $C_4A\bar{C}H_{11}$ 2.86; $C_4AH_{13}$ 2.86
2.80	C-S-H
2.77	Alite and Belite, Hydrogarnet, Ettringite
2.75-2.74	Alite and Belite; $C_4A\bar{S}H_{12}$ 2.72
2.70	$C_3A$ ; 2.69 of $C_4AH_{13}$
2.63-2.68	Aluminoferrite solid solutions
2.628	CH I = 100
2.564	Ettringite
2.54	Belite, $C_4A\bar{C}_{0.5}H_{12}$ , 2.53 of Hydrogarnet; 2.524 $C_4A\bar{C}H_{11}$ <sup>(7)</sup>
2.495	Calcite, $C_4AH_{13}$ , $C_4A\bar{C}H_{11}$
2.47	$C_4AH_{13}$
2.45	$C_4AH_{13}$ , $C_4A\bar{S}H_{12}$ , $C_4A\bar{C}_{0.5}H_{12}$
2.42	$C_4A\bar{S}H_{12}$ , $C_4A\bar{C}H_{11}$
2.40	CaO - improbable in paste
2.35	$C_4A\bar{C}_{0.5}H_{12}$ , 2.34 of $C_4A\bar{C}H_{11}$
2.285	Calcite - weak
2.27	Hydrogarnet, I = 100; 2.26 of $C_4A\bar{S}H_{12}$
2.23	Ettringite, $C_4A\bar{C}_{0.5}H_{12}$
2.209	Ettringite
2.185	Alite, Belite
2.169	Alite, Belite
2.10	MgO I = 100; 2.095 Calcite; 2.09 weak Alite, Belite
2.07	$C_4A\bar{S}H_{12}$
2.00	Hydrogarnet I = 95
1.927	CH

**Table 5. Continued.**

$d, m \times 10^{-10}$

1.796 CH

1.687 CH

1.66  $C_4\bar{A}\bar{S}\bar{H}_{12}$ ,  $C_4\bar{A}\bar{C}_{0.5}\bar{H}_{12}$ ,  $C_4\bar{A}\bar{C}\bar{H}_{11}$ ,  $C_4\bar{A}\bar{H}_{13}$

(1) Ettringite, H. E. Swanson, N. T. Gilfrich, M. I. Cook, R. Stinchfield, and P. C. Parks, Standard X-Ray Diffraction Powder Patterns, Vol 8, NBS Circular 539, p 3, 1959.

Calcium hydroxide, H. E. Swanson and E. Tatge, *ibid*, Vol 1, 1953, p 59; MgO, p 37, CaO, p 43, Calcite, H. E. Swanson and R. Fuyat, *ibid*, Vol 2, 1953, p 51.

(2) P. Seligmann and N. R. Greening, Studies of Early Hydration Reactions of Portland Cement by X-Ray Diffraction, Highway Research Record No. 62, pp 80-105, 1964.

(3)  $C_4\bar{A}\bar{S}\bar{H}_{12}$ , this program and H. F. W. Taylor, ed., The Chemistry of Cements, Vol 2, p 396, 1964.

(4) H. E. Schwiete and Udo Ludwig, Crystal Structures and Properties of Cement Hydration Products, Proc., Fifth Int. Sym. on Chem. of Cement, Tokyo, 1968, Vol II, pp 37-67, 1969;

(5) *ibid*, and this program;

(6) M. H. Roberts, Calcium aluminate hydrates and related basic salt solid solutions, *ibid*, pp 104-117.

(7) H. F. W. Taylor, The Chemistry of Cements, Vol 2, pp 347-404, 1964.

(8) Spacings from D. L. Kantro et al, An X-Ray diffraction investigation of hydrated portland cement pastes, Am Soc Testing Mats, Proc., Vol 60, pp 1020-1035, 1960. Intensities calculated from fig. in B. Marchese and R. Sersale, Stability of hydrogarnet series terms to sulphate attack, Proc., Fifth Int Sym on the Chemistry of Cement, Tokyo, 1968, Vol II, pp 133-137.

(9) Data from this program.

**Table 6. Cement No. 1: Constituents of pastes with w/c = 0.35.**

	Curing, Days				
	1	7	28	90	365
Ettringite	x	x	x	x	x
$C_4\bar{A}\bar{S}\bar{H}_{12}$	-	x	x	x	x
Calcium hydroxide	x	x	x	x	x
Hydrogarnet	-	tr?	tr?	x	x
$C_4\bar{A}\bar{C}\bar{H}_{11}$	-	-	-	x	tr
$C_4\bar{A}\bar{H}_x$	-	x	x	x	-
$C_3\bar{A}\bar{H}_6$	-	-	-	?	-
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
$C_3\bar{A}$	x	x	x	x	x
Aluminoferrite	x	x	x	x	x
MgO	x	x	x	x	x

NOTES: tr = trace; tr? = possible trace.

Laboratories Reporting Each Constituent

	6	6	5	5	2
Ettringite	6	6	5	5	2
$C_4\bar{A}\bar{S}\bar{H}_{12}$	-	4	4	6	3
Calcium hydroxide	7	7	7	7	6
Hydrogarnet	-	1	1	1	1
$C_4\bar{A}\bar{C}\bar{H}_{11}$	-	-	-	1	2
$C_4\bar{A}\bar{H}_x$ (Total of 2)	-	1	1	1	-
$C_3\bar{A}\bar{H}_6$	-	-	-	1	-
C-S-H	1	2	4	5	5
Alite	4	4	4	5	3
Belite	4	4	4	5	2
$C_3\bar{A}$	5	4	4	4	1
Aluminoferrite	4	4	4	4	2
MgO	4	4	4	5	3

**Table 7. Cement No. 2: Constituents of pastes with w/c = 0.35.**

	Curing, Days				
	1	7	28	90	365
Ettringite	x	x	x	x	tr?
$C_4\bar{A}\bar{S}\bar{H}_{12}$	tr?	x	x	x	x
Calcium hydroxide	x	x	x	x	x
Hydrogarnet	-	-	-	-	tr?
$C_4\bar{A}\bar{C}\bar{H}_{11}$	-	-	x	x	x
$C_4\bar{A}\bar{H}_x$ (3)	-	-	x	x	x
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
$C_3\bar{A}$	x	x	x	-	-

NOTE: tr? = possible trace.

Laboratories Reporting Each Constituent

	5	5	5	4	1
Ettringite	5	5	5	4	1
$C_4\bar{A}\bar{S}\bar{H}_{12}$	2	4	5	5	2
Calcium hydroxide	7	7	7	7	6
Hydrogarnet	-	-	-	-	1
$C_4\bar{A}\bar{C}\bar{H}_{11}$	-	-	2	3	-
$C_4\bar{A}\bar{H}_x$	-	-	1	1	1
C-S-H	1	2	4	5	4
Alite	5	5	5	5	3
Belite	5	5	5	4	3
$C_3\bar{A}$	5	2	2	-	-

**Table 8. Cement No. 3: Constituents of pastes with w/c = 0.35.**

	Curing, Days				
	1	7	28	90	365
Ettringite	x	x	x	x	tr
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	tr?	tr	tr	tr	tr?
Calcium hydroxide	x	x	x	x	x
C <sub>4</sub> AH <sub>x</sub>	tr	-	-	-	-
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
Aluminoferrite	x	x	x	x	x

NOTES: tr = trace; tr? = possible trace.

Laboratories Reporting Each Constituent

Ettringite	4	3	4	5	2
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	1	2	2	2	1
Calcium hydroxide	7	7	7	7	6
C <sub>4</sub> AH <sub>x</sub>	1	-	-	-	-
C-S-H	1	4	4	5	3
Alite	5	5	5	5	5
Belite	5	4	4	3	2
Aluminoferrite	6	6	6	6	6

**Table 9. Cement No. 1: Constituents of pastes of w/c = 0.65.**

	Curing, Days				
	1	7	28	90	365
Ettringite	x	x	x	x	-
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	x	x	x	x	x
Ca(OH) <sub>2</sub>	x	x	x	x	x
Hydrogarnet	tr?	tr	tr	tr	tr
C <sub>4</sub> AH <sub>x</sub>	-	-	P	D	-
C <sub>4</sub> A <sub>3</sub> H <sub>11</sub>	-	tr	x	x	tr
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
C <sub>3</sub> A	x	x	tr?	-	-
Aluminoferrite solid solution	x	x	x	x	x
MgO	x	x	x	x	x
Calcite	tr	tr	-	-	-

NOTES: tr? = possible trace; P = possible; D = doubtful.

Laboratories Reporting Each Constituent

Ettringite	6	4	4	4	-
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	1	6	5	6	5
Ca(OH) <sub>2</sub>	7	7	7	7	6
Hydrogarnet	1	2	2	2	2
C <sub>4</sub> AH <sub>x</sub>	-	-	1	1	-
C <sub>4</sub> A <sub>3</sub> H <sub>11</sub>	-	3	3	4	1
C-S-H	1	1	4	4	2
Alite	4	4	4	5	1
Belite	4	4	4	4	2
C <sub>3</sub> A	5	3	1	-	-
Aluminoferrite solid solution	4	4	4	4	1
MgO	4	4	4	5	2
Calcite	1	1	-	-	-

**Table 10. Cement No. 2: Constituents of pastes of w/c = 0.65.**

	Curing, Days				
	1	7	28	90	365
Ettringite	x	x	x	x	x
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	-	x	x	x	x
Ca(OH) <sub>2</sub>	x	x	x	x	x
C <sub>4</sub> AH <sub>x</sub>	-	-	-	-	x
C <sub>4</sub> A <sub>3</sub> H <sub>11</sub>	x	x	x	x	tr
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
C <sub>3</sub> A	x	x	x	x	-
Calcite	tr?	-	-	-	-

NOTES: tr = trace; tr? = possible trace.

Laboratories Reporting Each Constituent

Ettringite	6	5	5	4	4
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	-	7	7	6	5
Ca(OH) <sub>2</sub>	7	7	7	7	6
C <sub>4</sub> AH <sub>x</sub>	-	-	-	-	1
C <sub>4</sub> A <sub>3</sub> H <sub>11</sub> (Total of 3)	1	2	2	2	1
C-S-H	1	3	4	4	3
Alite	5	5	5	5	1
Belite	5	5	5	4	2
C <sub>3</sub> A	5	2	2	1	-
Calcite	1	-	-	-	-

**Table 11. Cement No. 3: Constituents of pastes of w/c = 0.65.**

	Curing, Days				
	1	7	28	90	365
Ettringite	x	x	x	x	x
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub>	-	tr	tr?	tr	?
Ca(OH) <sub>2</sub>	x	x	x	x	x
C <sub>4</sub> AH <sub>x</sub>	-	tr	-	tr	-
C <sub>4</sub> A <sub>3</sub> H <sub>11</sub>	-	-	-	-	tr?
C-S-H	x	x	x	x	x
Alite	x	x	x	x	tr
Belite	x	x	x	x	x
Aluminoferrite solid solution	x	x	x	x	x
Calcite	tr	tr	tr	tr	-

NOTES: tr = trace; tr? = possible trace.

Laboratories Reporting Each Constituent

Ettringite	4	4	4	4	2
C <sub>4</sub> A <sub>3</sub> H <sub>12</sub> (Total of 3)	-	2	1	2	1
Ca(OH) <sub>2</sub>	7	7	7	7	6
Hydrogarnet	1	1	-	-	-
C <sub>4</sub> AH <sub>x</sub>	-	1	-	1	-
C <sub>4</sub> A <sub>3</sub> H <sub>11</sub>	-	-	-	-	1
C-S-H	1	4	4	4	3
Alite	5	5	4	4	1
Belite	5	4	3	2	1
Aluminoferrite solid solution	6	6	6	6	5
Calcite	1	1	1	1	-

Figure 1. Partial diffractometer charts of pastes of 0.65 w/c, cement No. 1. Beam slit 1 deg, 3 deg beam slit as Soller, 0.2 deg detector slit, scanning speed 0.2 deg per minute, linear rate meter operation with full scale deflection 1,000 counts per second, time constant 8 sec; MS =  $C_4A\bar{S}H_{12}$ . MC =  $C_4A\bar{C}H_{11}$ . HG = hydrogarnet.

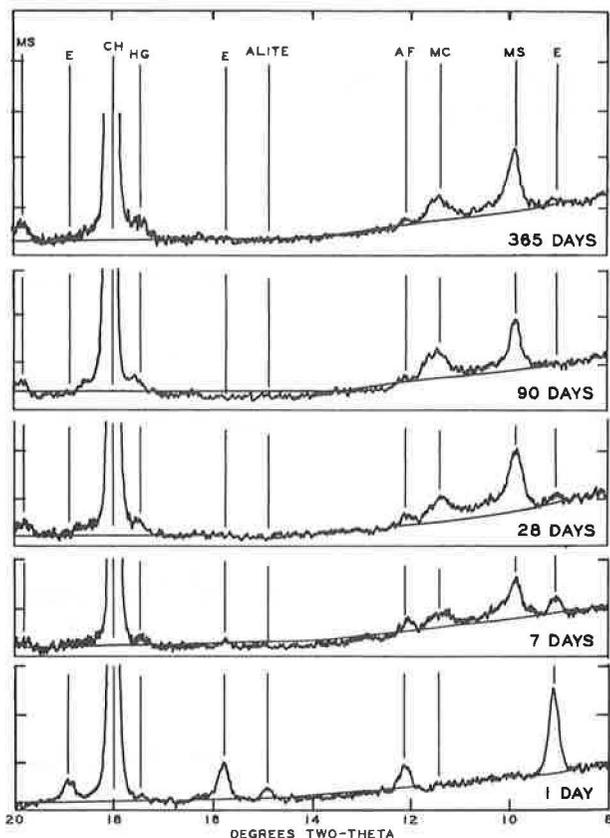


Figure 2. Partial diffractometer charts of pastes of 0.65 w/c, cement No. 2, as in Figure 1. The hydrogarnet line at 17.5 two-theta is shown, but evidence of its presence is suggested only at 7 days. The broad indefinite bulge marked MC(= $C_4A\bar{C}H_{11}$ ) in charts of 7 through 90 day pastes covers a range of spacings and alternate identifications could be made.

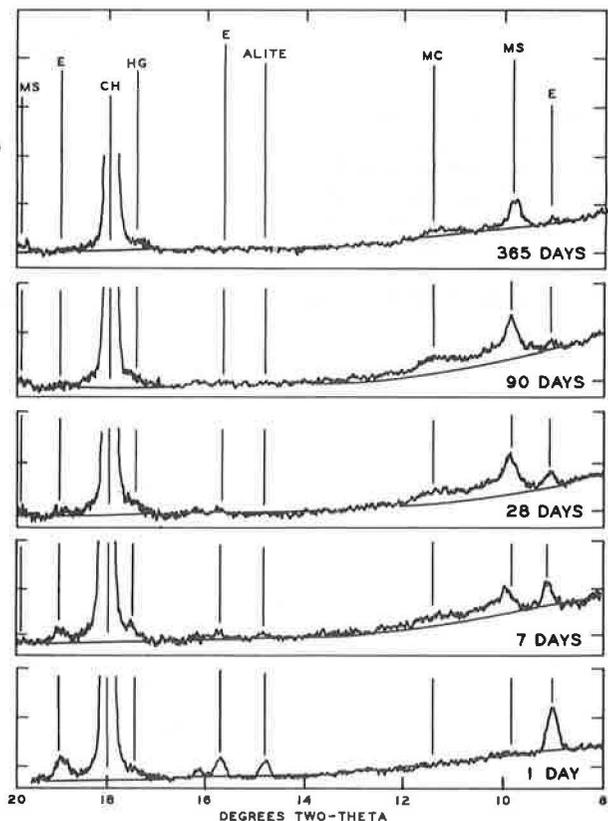


Figure 3. Charts of pastes of 0.65 w/c, cement No. 3, as in Figures 1 and 2.

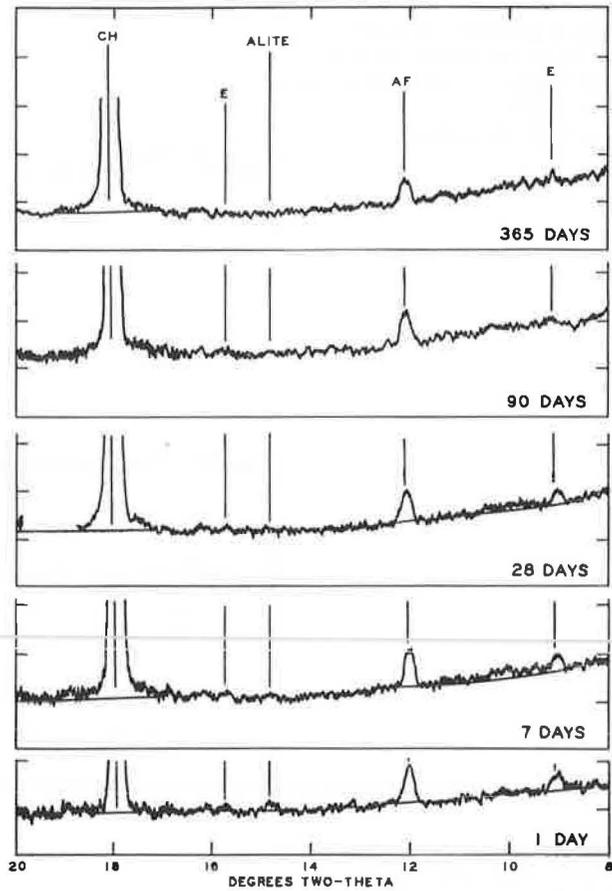


Figure 4. Partial diffractometer charts of 365-day pastes, cement No. 1. Conditions as in Figures 1 through 3 except logarithmic rate meter operation with time constants 30, 7.5, and 2 sec in the first, second, and third decades of the scale. Residual silicates present in 0.35 w/c paste.

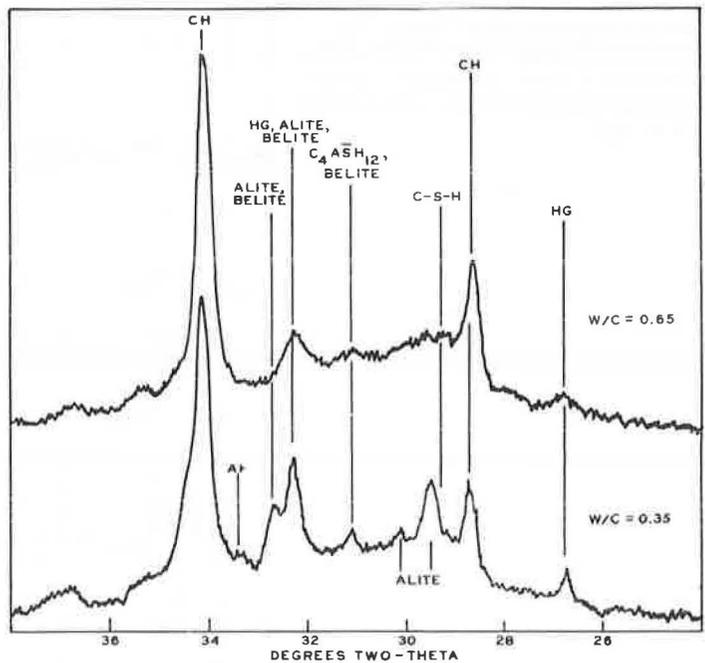


Figure 5. Charts of 365-day pastes of cement No. 2. Both pastes contain some residual silicates.

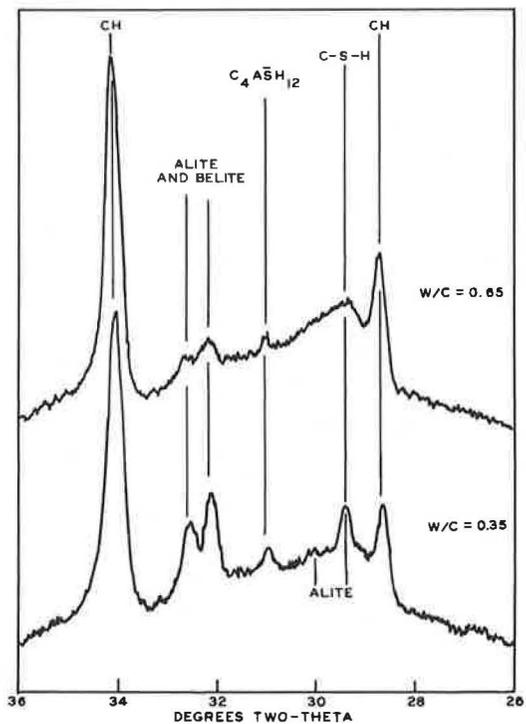
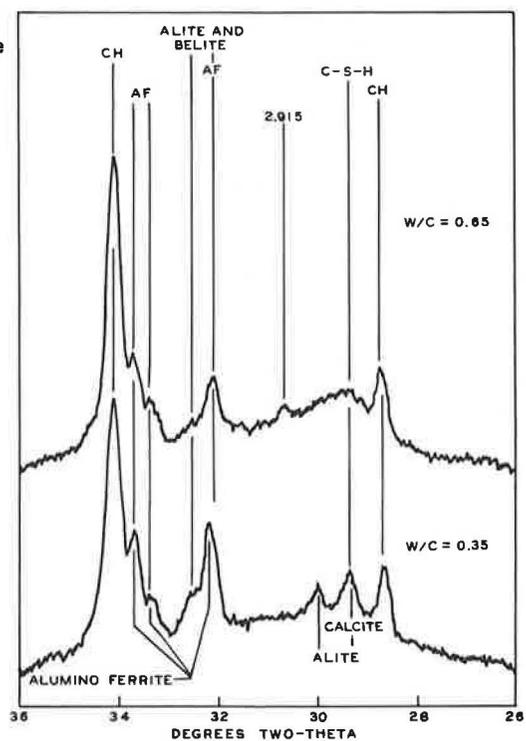


Figure 6. Charts of 365-day pastes of cement No. 3. Strong residual aluminoferrite solid solutions and some silicates. Spacing at 2.915 Å unidentified.



All the participating laboratories reported the presence of calcium hydroxide in pastes of all three cements, at both water-cement ratios and at all ages. Ettringite was reported in pastes of all three cements at both water-cement ratios at all ages with one exception; none was reported in pastes of cement No. 1 of 0.65 water-cement at 365 days (Figs. 1-3).  $C_4ASH_{12}$  was reported in pastes of all three cements at 0.35 water-cement ratio at all ages with two exceptions: none was reported in pastes of cement No. 1 or No. 3 at 1 day; only two laboratories reported it in pastes of cement No. 3. Both indicated that it was present in small amounts only. In pastes of 0.65 water-cement ratio,  $C_4ASH_{12}$  was reported from cement No. 1 at all ages, and from cement Nos. 2 and 3 at all ages except 1 day. Again, only two laboratories reported it from pastes of Cement No. 3. Judging by the number of laboratories reporting its presence in pastes of cement No. 2 with 0.65 water-cement ratio at ages greater than 1 day, these pastes contained more  $C_4ASH_{12}$  than any others in the program (Figs. 1-5). Hydrogarnet was reported by only two laboratories; one reported it in pastes of cement No. 1 with 0.35 water-cement ratio at ages of 7 through 365 days; in pastes of the same cement with water-cement ratio of 0.65 one laboratory reported it at 1 day and two at all later ages. Apparently it formed more abundantly or more recognizably in pastes with the higher water-cement ratio (Figs. 1 and 4). In pastes of cement No. 2 with 0.35 water-cement ratio it was reported by one laboratory at 365 days. In pastes of cement No. 3 with 0.65 water-cement ratio it was reported by one laboratory at 1 and 7 days, and not thereafter. Kantro, Copeland, and Anderson<sup>10</sup> reported hydrogarnet in pastes of cements of several types; it has also been reported from field concretes.<sup>12</sup>

C-S-H gel was reported in pastes of all cements, at both water-cement ratios, by one to five laboratories.

Three other hydrates were reported:  $C_4ACH_{11}$ ,  $C_4AH_x$ , and  $C_3AH_6$ . The first was reported at one or more ages in pastes with both water-cement ratios from cements No. 1 and 2; it was not reported from pastes of cement No. 3 except in pastes of 0.65 water-cement ratio at 365 days. It appears that when it formed, it formed more abundantly from pastes of 0.65 water-cement ratio. It was least abundant in pastes of cement No. 3 in which less ettringite developed than in pastes of cements 1 and 2.  $C_4AH_x$ , characterized by a line at 7.9 A, was reported by two laboratories at one or more ages in the pastes of 0.35 water-cement ratio of all three cements, and by one in the pastes of 0.65 water-cement ratio of cements No. 2 and 3. Another laboratory reported it from pastes of cement No. 1 of 0.65 water-cement ratio at two ages. One laboratory reported  $C_3AH_6$  in paste of cement No. 1 with 0.35 w/c at one age as doubtful.

Unhydrated constituents of all cements were reported. Alite was reported from all pastes at all ages, but in pastes of 0.65 water-cement ratio the number of laboratories reporting it fell off sharply at 365 days. Belite was also reported from all pastes at all ages. Aluminoferrite solid solution was reported in pastes of cements 1 and 3 at both water-cement ratios at all ages. MgO was reported only from Cement No. 1 in pastes of both water ratios at all ages.  $C_3A$  was reported in pastes of cement 1 at 0.35 w/c at all ages, and through 28 days in pastes of 0.65 w/c. It was reported through 28 days in pastes of cement No. 2 at 0.35 water-cement ratio and through 90 days in pastes of 0.65 water-cement ratio.

One laboratory reported calcite at one or more ages in pastes of all three cements at 0.65 water-cement ratio.

One laboratory compared diffractometer traces made with the same operating conditions for each cement at each water-cement ratio and age to see what effects of water-cement ratio could be detected. With logarithmic operation of the rate meter and full scale deflection equal to 4000 counts per sec, beam slit 1 deg, 3 deg beam slit as Soller, and 0.2 detector slit:

(1) Background levels in pastes of cement No. 1 and No. 2 were lower than in pastes of cement No. 3.

(2) The heights of the calcium hydroxide peaks at 18 and 34 deg two-theta increased in pastes cured longer than 1 day, and were greater in the pastes of higher water-cement ratio. The net intensity of these peaks was less in cement No. 3 than in pastes of the other two cements.

(3) Age by age, the pastes of 0.35 water-cement ratio contained more conspicuous remains of the structure of the unhydrated cement.

(4) In pastes of cement No. 1 CH was more abundant in those of 0.65 w/c. Ettringite was more abundant in pastes at 0.65 water content at 1 and 7 days, less abundant at 28, 90, and 365 days.  $C_4ASH_{12}$  was more abundant at 7, 28, 90, and 365 days in pastes of 0.65 water-cement ratio. Hydrogarnet increased from 7 days through 365 days in the pastes of 0.65 water-cement ratio. If the lines at 5.94, 2.97, and 1.76 A are taken as unequivocal evidence of the presence of alite, the 5.94 A line was

recognizable in the pastes of 0.35 w/c through 28 days but was only present at 1 day in those of 0.65 w/c; the line at 2.97 A is recognizable but very very weak at 365 days, and the line at 1.76 A is present through 365 days in the pastes of lower w/c. In the pastes of 0.65 water-cement ratio the line at 1.76 is perceptible through 28 days but that at 2.97 A is not. The 2.70 A line of  $C_3A$  is probably present at 7 days, but not thereafter, in the paste of 0.65 water-cement ratio; in the 0.35 w/c pastes it is present at 28 days, but thereafter only the aluminoferrite line at 2.683 A can be recognized. At both water cement ratios, MgO decreased from 1 to 7 days but did not change thereafter. In the pastes of both water-cement ratios the 2.88 A peak appeared to increase from 7 days over what it was at 1 day, showing the presence of  $C_4ASH_{12}$  and rendering the peak only dubious evidence of belite. The aluminoferrite line at 12 deg two-theta was present at all ages in pastes of 0.35 and 0.65 water cement ratio.

(5) In pastes of cement No. 2, with both water-cement ratios, the apparent intensities of the calcium hydroxide line at 4.92 A increase with age. The ettringite lines are more intense in the pastes of 0.65 water-cement ratio through 90 days;  $C_4ASH_{12}$  is present at 1 day in the pastes of 0.65 water-cement ratio and increases thereafter to 90 days, diminishing apparently at 365 days. The 2.88 A line diminishes from 1 day through 90 days and then increases at 365 days in the pastes of 0.65 water-cement ratio. In the pastes of 0.35 water-cement ratio, the 2.88 A line increases from 7 days, showing the increase in  $C_4ASH_{12}$  but making the spacing dubious as evidence of belite. The  $C_3A$  line at 2.70 A persisted to 7 days in the pastes of lower water-cement ratio and was detectable at 1 day in the 0.65 water-cement ratio paste. In the paste of lower water-cement ratio the 2.97 A and 1.76 A lines of alite persisted at 365 days; in the paste of higher water content, the 2.97 A line was not recognized at 90 days, the 1.76 line was detectable at 90 but not at 365 days.

(6) Pastes of cement No. 3 at both water contents contained ettringite at all ages.  $C_4ASH_{12}$  could be detected in pastes cured more than 1 day, but it was less conspicuous than the ettringite. The belite line at 2.88 A was barely perceptible at 7 days in the paste of higher water content but persisted until 28 days in the paste of lower water content. The alite lines at 2.97 A and 1.76 A were detected at 365 days in pastes of lower water content; the 2.97 A line was detected at 28 days, and the 1.76 A line was barely detected at 90 days in the paste of higher water content. Aluminoferrite lines, including the weak line at 3.66 A, persisted at 365 days in pastes of both water contents.

Table 12 shows scaled intensities of characteristic peaks of ettringite,  $C_4ASH_{12}$  and calcium hydroxide of pastes of all three cements at 0.65 water-cement ratio.

### Examination of Hydrates and Synthetic Products

Two reports of spacings of hydrated alite cured 5.3 years appear in Table 13. It contained calcium hydroxide and C-S-H gel, represented by broad lines at 3.07 A and 1.82 A (Fig. 7). Laboratory 6 reported a line at 2.97 A, not resolved by laboratory 3, and identified it as another C-S-H gel spacing. Laboratory 3 described the spacing at 3.066 A as a broad asymmetric hump from about 26 to 38 degrees two-theta, rising steeply from 28 to 29.3 degrees and then sloping gently to background at 38 degrees. The spacing at 1.819 A was described as a symmetrical hump about 2.5 two-theta broad at the background level. No residual lines of unhydrated alite were found by any of the participants, and the third spacing of near-amorphous C-S-H gel at about 2.80 A was apparently inconspicuous.

The hydrated  $\beta C_2S$  (Table 14) contained less calcium hydroxide, a large number of spacings characteristic of unhydrated  $\beta C_2S$ , and the spacing at 2.97 A (reported by three laboratories) identified by laboratory 6 as C-S-H gel, as well as spacings at 3.05 or 3.06 A, 2.815 A (?) or 2.79 A, and 1.819 A, or 1.825 A, characteristic of the almost amorphous C-S-H gel.

Three hexagonal platy calcium aluminate hydrates with additional anions were examined by most of the participating laboratories. Results are reported in Tables 15 through 17.

$C_4AC_0.5H_{12}$  was examined in six laboratories; in four of these the samples contained  $C_4AC_0.5H_{10}$  as well as  $C_4AC_0.5H_{12}$ . It also contained a small amount of  $C_3AH_6$ . Dosch and zur Strassen<sup>13</sup> obtained  $C_4AC_0.5H_{12}$  with a basal spacing of 8.2 A at 81 percent relative humidity and a dehydration product with a basal spacing of 7.7 A and a water content recorded as 9 H<sub>2</sub>O at 11 percent relative humidity; it appears they did not investigate the production of the partially dehydrated phase at higher humidities. Since the 7.7 A phase appeared in the results of four laboratories, it seems probable that dehydration of the 8.2 A phase begins at relative humidities above 11 percent.

**Table 12. Intensity relations among some constituents of pastes of 0.65 water-cement ratio<sup>1</sup>.**

	Peak Height Above Background, Counts/Second				
	Age, days				
	1	7	28	90	365
<b>Cement No. 1 - Type 1</b>					
Ettringite	87	21	<5 (est)	tr (est)	-
C <sub>4</sub> A\$H <sub>12</sub>	-	41	72	74	58
C <sub>4</sub> A\$H <sub>11</sub> (Note 2)	-	pr	pr	pr	pr
CH	489	417	702	842	679
<b>Cement No. 2 - White</b>					
Ettringite	47	28	18	5 (est)	tr
C <sub>4</sub> A\$H <sub>12</sub>	-	26	39	41	34
C <sub>4</sub> A\$H <sub>11</sub>	-	tr?	tr	pr	pr
CH	653	848	692	492	435
<b>Cement No. 3 - Zero C<sub>4</sub>A</b>					
Ettringite	20	20	20	5 (est)	<5 (est)
C <sub>4</sub> A\$H <sub>12</sub>	-	tr	tr?	tr	?
CH	460	986	1019	752	821

(1) Determined by scaling peak heights and adjoining background with diffraction conditions as follows: 50 KVCP and 21 ma, Cu radiation with M filter, 1° Beam Slit, 3° BS as Soller, 0.2° detector slit, full scale deflection of chart 1000 counts, linear rate meter operation, time constant 8 sec, December 1966. Peaks scaled were 9.7 Å (ettringite), 8.98 Å (C<sub>4</sub>A\$H<sub>12</sub>), and 4.92 Å (CH).

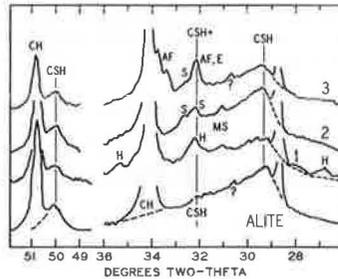
(2) C<sub>4</sub>A\$H<sub>11</sub> was not scaled but its presence is noted as trace, possible trace, or present.

**Table 13. Sample 35: Hydrated alite cured 5.3 years.**

Laboratory 3			Laboratory 6		
d, Å	I%		d, Å	I	
4.92	83	CH	4.9	vs	CH
3.114	28	CH	3.12	ms	CH
3.066	12	C-S-H**	3.07	m/b	C-S-H
			2.98	vvw	C-S-H
2.786	5	C-S-H	2.83	vvw	?
2.629	100	CH	2.63	vvv	CH
			2.46	vvw	CH
1.926	43	CH	1.93	vs	CH
1.819	5	C-S-H***	1.83	w	C-S-H
1.796	29	CH	1.80	vs	CH
1.686	15	CH	1.69	s	CH
1.635	1	CH	1.64	vw	CH
1.554	2	CH	1.56	m	CH
1.483	7	CH			
1.449	7	CH			

A Nel peak height referred to net height of most intense peak as 100.  
 \*\* Hump from 26 to 38 two-theta, falling off steeply from 29.3 to 28 two-theta.  
 \*\*\* About 2.5 two-theta wide at the base.

**Figure 7. Charts of 0.65 w/c 365-day pastes of all three cements, with 5.3-year-hydrated alite as comparison. The alite spacing between 29 and 30 deg appears longer than those of the cements. C-S-H = C-S-H gel; S = silicates (alite and belite).**



**Table 14. Sample 36: Hydrated  $\beta$ -C<sub>2</sub>S cured 5.3 years.**

Laboratory 3			Laboratory 6		
d, Å	I*		d, Å	I	
4.91	100	CH	4.91	ms	CH
4.64	1	$\beta$ -C <sub>2</sub> S			
3.23	2	$\beta$ -C <sub>2</sub> S	3.34	vw	C <sub>2</sub> S
3.11	16	CH	3.11	ms	CH
3.052	31	C-S-H, CaCO <sub>3</sub> ?**	3.06	ms/b	C-S-H
2.966	21		2.97	w/b	C-S-H
2.877	16	$\beta$ -C <sub>2</sub> S	2.88	mw	C <sub>2</sub> S
2.815	17	?			
2.781	21	$\beta$ -C <sub>2</sub> S	2.79	m	C <sub>2</sub> S, C-S-H
2.739	19	$\beta$ -C <sub>2</sub> S	2.75	w	C <sub>2</sub> S
2.720	10	$\beta$ -C <sub>2</sub> S			
2.627	60	CH	2.63	vvvs	CH
			2.61	w	C <sub>2</sub> S
2.547	2	$\beta$ -C <sub>2</sub> S			
2.442	4	$\beta$ -C <sub>2</sub> S, CH	2.44	w	CH, C <sub>2</sub> S
2.404	4	$\beta$ -C <sub>2</sub> S	2.41	vw	C-S-H, C <sub>2</sub> S
2.279	3	$\beta$ -C <sub>2</sub> S	2.28	w	C <sub>2</sub> S
2.189	7	$\beta$ -C <sub>2</sub> S	2.19	mw	C <sub>2</sub> S
2.164	2	$\beta$ -C <sub>2</sub> S	2.165	vw	C <sub>2</sub> S
2.130	1	$\beta$ -C <sub>2</sub> S			
2.088	2	$\beta$ -C <sub>2</sub> S	2.08	vvw	C <sub>2</sub> S
			2.05	vvw	C <sub>2</sub> S
2.026	3	$\beta$ -C <sub>2</sub> S			
1.984	4	$\beta$ -C <sub>2</sub> S, CH	1.98	vw	C <sub>2</sub> S
1.926	23	CH	1.93	ms	CH
1.894	2	$\beta$ -C <sub>2</sub> S			
1.819	12	C-S-H***	1.825	ms/b	C-S-H
1.796	9	CH	1.799	s	CH
1.707	1	$\beta$ -C <sub>2</sub> S			
1.685	6	CH	1.69	m	CH
1.627	1	$\beta$ -C <sub>2</sub> S	1.628	w	CH
1.549	2	$\beta$ -C <sub>2</sub> S			
1.524	2	$\beta$ -C <sub>2</sub> S			
1.482	3	CH			
1.448	3	CH			

\* Net peak height referred to net peak height of strongest peak as 100.

\*\* K<sub>1</sub> from 26 to 38 two-theta.

\*\*\* About 2 two-theta wide at base.

**Table 15. Sample 37: Tetracalcium aluminate hemihydrate-12-hydrate.**

Laboratory 5		Laboratory 6	
d, Å	I	d, Å	I
8.12	vvvs	8.2	10
		7.8	1
			?
5.405	vw		
5.12	w	5.11	3
4.895	w		
		4.62	4
		4.43	2
4.104	vs	4.09	7
3.878	s	3.87	9
		3.77	1
		3.50	2
3.359	w	3.35	2
3.245	vw		
3.134	vw	3.13	2
		3.02	1
2.88	m	2.88	9
		2.83	3
2.808	w	2.80	3
2.728	m	2.72	8
		2.62	2
2.549	m	2.54	8
		2.47	1
2.448	m	2.44	9
2.358	m	2.35	6
2.319	w	2.31	4
2.293	ms	2.29	3
		2.22	4
		2.20	2
2.166	w	2.16	2
		2.07	1
2.043	m	2.03	5
1.985	m	1.98	4
1.939	w	1.94	3
		1.88	1
		1.86	5
		1.85	5
		1.80	1
1.771	w	1.78	1
1.75	w	1.75	3
		1.74	3
		1.70	1
		1.68	1
		1.67	1
1.663	w	1.66	8
1.635	w	1.63	7

7 more lines to 1.42

**Table 16. Sample 38: Tetracalcium aluminate carbonate-11-hydrate.**

Laboratory 3		Laboratory 6	
d,Å	I <sup>o</sup>	d,Å	I
7.62	100	7.6	10
5.71	<1	5.72	1
5.14	<1	5.12	2
4.98	<1	4.94	1
4.85	1	4.88	1
		4.82	1
4.68	<1	4.66	2
4.49	1	4.46	3
4.36	2	4.34	4
3.99	2	3.97	5
		3.81	5
3.79	47	3.80	8
3.65	1	3.64	3
3.46	3	3.45	5
		3.40	1
3.36	<1	3.34	1
3.30	<1	3.29	1
3.144	<1	3.13	1
3.03	<1	2.89	9
2.859	7	2.85	9
		2.82	3
		2.81	1
2.779	2	2.70	5
2.725	4	2.73	7
2.654	1	2.65	1
		2.62	1
2.576	<1	2.58	2
2.526	9	2.53	7
		2.52	2
2.490	5	2.49	6
		2.48	7
2.444	3	2.44	6
2.422	11	2.42	6
2.340	11	2.33	6
2.294	2	2.29	3
		2.26	1
2.239	1	2.23	1
2.214	<1	2.21	3
2.167	5	2.165	1
		2.16	3
2.140	<1	2.13	2
2.118	5	2.11	5
2.099	5	2.09	3
2.065	<1	2.06	2
2.036	2	2.03	2
2.028	2	2.02	1
2.013	3	2.01	3
1.992	<1	1.99	2
1.946	6	1.94	4
		1.93	2
1.906	<1	1.90	2
1.892	1	1.88	2
1.861	3	1.86	4
		1.83	1
1.824	4	1.82	4
1.796	<1	1.80	1
		1.77	1
1.751	<1	1.75	1
1.745	<1	1.74	1
1.728	<1	1.72	1
1.714	1	1.71	1
1.690	<1	1.69	1
1.679	<1	1.68	1
1.665	2	1.67	1
		1.66	5

and five lines to 1.60

\* Intensity expressed as net peak height referred to height of 7.62-Å peak.

**Table 17. Sample 39: Tetracalcium aluminate monosulfate-12-hydrate.**

Laboratory 3		Laboratory 6			
d,Å	I <sup>o</sup>	d,Å	I		
9.8	2	9.8	1		
				Ettringite	
8.96	100	9.0	10		
5.60	<1	5.62	1		
4.90	1	4.92	3		
4.68	<1	4.70	1		
4.47	32	4.48	8		
4.00	12	4.00	9		
3.88	<1	3.88	1		
3.65	1	3.66	3		
				E	
3.47	<1	3.48	1		
3.24	<1			E	
3.031	<1			Calcite	
2.879	6	2.88	9		
2.778	1	2.78	1		
2.741	3	2.74	6		
2.615	<1	2.63	1		
2.559	<1	2.56	1		
2.479	<1	2.48	2		
2.449	4	2.45	8		
2.421	8	2.42	8		
2.362	4	2.36	2		
2.336	2	2.34	4		
2.260	1	2.26	3		
2.236	2	2.24	1		
2.189	4	2.20	1		
		2.19	3		
2.149	<1	2.15	1		
2.088	1	2.09	2		
2.072	6	2.07	6		
2.000	1	2.00	3		
1.905	2	1.91	2		
1.874	<1	1.88	2		
1.867	<1	1.87	2		
1.825	3	1.83	4		
1.816	1	1.81	3		
1.788	<1	1.78	2		
1.765	1	1.77	2		
1.742	<1	1.74	1		
1.691	<1	1.69	1		
1.661	2	1.66	7		
1.634	1	1.64	1		
		1.63	5		
1.589	2	1.59	2		
1.558	<1	1.56	3		
1.544	<1	1.54	3		
1.522	<1			E	
1.504	<1			E	
1.492	<1	1.49	2		
1.454	<1	1.45	1		
1.439	<1	1.44	3		
1.422	<1	1.42	2		
1.392	2	1.39	2		
		1.38	1		
		1.37	2		
		1.35	2		

\* Intensity expressed as net peak height referred to net peak height of 8.96 Å peak.

Dosch, Keller, and zur Strassen<sup>14</sup> have found that the carbonate content of the material described by Seligmann and Greening<sup>15</sup> as  $C_3A \cdot 1/2CA(OH)_2 \cdot 1/2CaCO_3 \cdot H_x$  (equal to  $C_4AC_0.5H_x$ ), ranges from 0.25 to 0.5, which reconciles the previous disparity of views on the carbonate content of the substance.

Table 16 shows spacings of  $C_4ACH_{11}$  reported by two laboratories. Very small amounts of  $C_3AH_6$  were reported by four of the six laboratories that examined this sample. There was no indication that any dehydration stage of  $C_4ACH_{11}$  was present.

Spacings of tetracalcium aluminatemonosulfate-12-hydrate ( $C_4ASH_{12}$ ) recorded by two laboratories are shown in Table 17. Five laboratories examined this sample; all found a small amount of ettringite with the monosulfate. Partial dehydration of the sample occurred in three of the laboratories; in two it took place because the sample was stored or examined at reduced relative humidity, but in the third it apparently resulted from laboratory ambient relative humidity. In one laboratory it was stored over  $CaCl_2 \cdot 2H_2O$  (at a relative humidity of 33 percent) for three days before X-ray examination. In another it was first examined in a static nitrogen atmosphere--in which it was partly dehydrated--and subsequently rehydrated by storing it in a sealed container for one week over  $Mg(NO_3)_2 \cdot 6H_2O$ , which produces a relative humidity over 50 percent at about 23 C (55% r.h. at 18 C, 21.5% at 31 C); this treatment returned all the sample to the 12-hydrate condition.

Sample 40 was prepared to have the composition  $C_4AH_{10.5}$ . Judging from the results of five laboratories, it appears to have been unstable. Reports from three laboratories are shown in Table 18, with interpretations provided by the writer. A summary of all five reports follows:

Laboratory		Laboratory	
1	$C_4AH_{13}$ , $C_4ACH_{11}$ ; $C_3AH_6$ , CH	3	$C_4AC_0.5H_{12}$ ; $C_3AH_6$ , CH
2	$C_4AH_{13}$ ; $C_3AH_6$ , CH	5	$C_4AC_0.5H_{12}$ , $C_4AC_0.5H_{10}$ ; $C_3AH_6$ , CH
		6	$C_4AC_0.5H_{12}$ , $C_4AH_{13}$ ; $C_3AH_6$ , CH

Carbonation and dehydration affected the portions of the sample differently in four of the laboratories.

Sample 41, ettringite produced at the National Bureau of Standards, was examined by five laboratories; results from two appear in Table 19. One laboratory examined another sample of ettringite prepared by the Portland Cement Association Research and Development Laboratories and found it comparable to the sample prepared by the National Bureau of Standards with the addition of two or three weak lines. Card 9-414, Ettringite, in the Powder Diffraction File<sup>16</sup> lists spacings from 9.73 to 1.768 A, including a total of 50. Participants in this program reported from 21 to 54 spacings in this range, including a few not shown on the card which are believed to represent one or more additional constituents of the sample. Moore and Taylor<sup>17</sup> have described the structure of naturally occurring ettringite from Scawt Hill. The crystal symmetry is trigonal with space group P31c; some crystals are hexagonal either because of partial disorder or twinning. The authors regard disorder as the more probable explanation.

One laboratory examined a sample prepared to represent a solid solution between  $C_4ASH_{12}$  and  $C_4AH_{13}$  with  $SO_3$  to  $Al_2O_3$  as 0.75 to 1.00. The constituents recognized were  $C_4ASH_{12}$ ,  $C_4ASH_{10}$ , and  $C_4ACH_{11}$ , although the sample was examined in a chamber which had an atmosphere above 90 percent relative humidity.

#### Discussion: Detection of C-S-H Gel

The results of examination of the hydrated silicates appear to show that C-S-H gel produced by the paste hydration of alite or  $\beta$ - $C_2S$  for 5.3 years yields broad weak spacings at about 3.05 to 3.07 A and 1.82 A, with the more intense at 3.05-3.07 A asymmetric, dropping steeply toward lower diffraction angles and tailing off gently to about 38 degrees two-theta; the third spacing at 2.8 A reported for nearly amorphous calcium silicate by Taylor<sup>18</sup> was not conspicuous in the hydrated alite (Table 13, Fig. 7) examined in this program and was masked in the hydrated  $\beta$ - $C_2S$  by residual unhydrated material. The cement pastes of 0.65 w/c hydrated for 1 year (Fig. 7) had the 2.80 A spacing masked in part by hydrogarnet and unhydrated silicates (cement No. 1), by residual unhydrated silicates (cement No. 2), and by residual silicates and aluminoferrites (cement No. 3). The pastes of 0.35 w/c at 365 days retained more unhydrated material, and accordingly the 2.8A spacing was not detected.

It appears to the writer that the results with respect to detection of C-S-H gel show the success of three approaches followed by participants. These are:

- (1) Use of the Guinier camera
- (2) Use of a diffractometer with a wide detector slit (beam slit 3°, 3° beam slit as Soller, 0.2° detector slit), at a scanning speed of 0.2° per minute with

Table 18. Unstable C<sub>4</sub>AH<sub>10.5</sub>.

Laboratory 1			Laboratory 3			Laboratory 5		
d, Å	I		d, Å	I		d, Å	I	
7.91	100	C <sub>4</sub> AH <sub>13</sub>	8.20	100	H	8.19	ss	H
7.60	7	H				7.81	s	C <sub>4</sub> AC <sub>0.5</sub> H <sub>10</sub>
			5.25	<1				
5.13	2	C <sub>3</sub> AH <sub>6</sub>	5.12	16	C <sub>3</sub> AH <sub>6</sub>	5.13	s	C <sub>3</sub> AH <sub>6</sub>
4.91	<1	CH	4.89	28	CH	4.91	s	CH
			4.62	<1	H	4.785	vw	H
4.44	<1	C <sub>3</sub> AH <sub>6</sub>	4.43	7	C <sub>3</sub> AH <sub>6</sub>	4.440	m	C <sub>3</sub> AH <sub>6</sub>
			4.09	28	H	4.105	s	H
3.96	22	C <sub>4</sub> AH <sub>13</sub>						
3.78	2	H	3.86	4	H	3.870	b	H
			3.50	<1	H			
3.36	1	C <sub>3</sub> AH <sub>6</sub>	3.348	8	C <sub>3</sub> AH <sub>6</sub>	3.336	m	C <sub>3</sub> AH <sub>6</sub>
			3.248	<1				
			3.136	6	C <sub>3</sub> AH <sub>6</sub>	3.140	w	C <sub>3</sub> AH <sub>6</sub>
			3.11	2	CH	3.115	w	CH
			2.879	2	H	2.880	vw	H
2.81	1	C <sub>3</sub> AH <sub>6</sub>	2.806	12	C <sub>3</sub> AH <sub>6</sub>	2.813	m	C <sub>3</sub> AH <sub>6</sub>
						2.731	vw	
			2.712	1	H			
			2.676	1	C <sub>3</sub> AH <sub>6</sub>	2.682	vw	C <sub>3</sub> AH <sub>6</sub>
2.64	1	CH	2.624	8	CH, H	2.629	m	CH, H
			2.562	3	C <sub>3</sub> AH <sub>6</sub>	2.571	w	C <sub>3</sub> AH <sub>6</sub>
			2.540	2	H			
2.47	1	C <sub>3</sub> AH <sub>6</sub>	2.460	5	C <sub>3</sub> AH <sub>6</sub>	2.469	w	C <sub>3</sub> AH <sub>6</sub>
			2.443	3	H, CH			
			2.350	1	H			
2.30	2	C <sub>3</sub> AH <sub>6</sub>	2.290	16	C <sub>3</sub> AH <sub>6</sub>	2.298	m	C <sub>3</sub> AH <sub>6</sub>
			2.210	2	C <sub>3</sub> AH <sub>6</sub> , H	2.209	b	C <sub>3</sub> AH <sub>6</sub>
			2.161	<1	H			
			2.116	<1				
2.04	2	C <sub>3</sub> AH <sub>6</sub>	2.036	15	C <sub>3</sub> AH <sub>6</sub> , H	2.040	b	C <sub>3</sub> AH <sub>6</sub> , H
1.98	1	C <sub>3</sub> AH <sub>6</sub>	1.984	2	C <sub>3</sub> AH <sub>6</sub> , H	1.987	vw	C <sub>3</sub> AH <sub>6</sub> , H
			1.922	5	CH	1.926	w	CH
			1.859	<1	H			
			1.831	<1	H			
			1.810	3	C <sub>3</sub> AH <sub>6</sub> , H	1.814	w	C <sub>3</sub> AH <sub>6</sub>
			1.792	1	H, CH	1.796	vw	
			1.774	<1	H	1.776	vw	H
1.74	<1	C <sub>3</sub> AH <sub>6</sub> , H	1.740	6	C <sub>3</sub> AH <sub>6</sub> , H	1.745	w	C <sub>3</sub> AH <sub>6</sub> , H
			1.707	4	C <sub>3</sub> AH <sub>6</sub>	1.711	w	
1.68	<1	C <sub>3</sub> AH <sub>6</sub>	1.676	9	C <sub>3</sub> AH <sub>6</sub> , CH	1.680	m	C <sub>3</sub> AH <sub>6</sub>
			1.662	1	H			
			1.630	<1	H			
			1.594	2	C <sub>3</sub> AH <sub>6</sub>	1.597	vw	C <sub>3</sub> AH <sub>6</sub>
			1.574	1	C <sub>3</sub> AH <sub>6</sub>	1.572	vw	C <sub>3</sub> AH <sub>6</sub>
			1.540	<1	H			
			1.522	<1	H	1.482		
			1.500	<1	H			
			1.480	1	C <sub>3</sub> AH <sub>6</sub> , CH	1.482	vw	C <sub>3</sub> AH <sub>6</sub> , CH

NOTE: H = C<sub>4</sub>AC<sub>0.5</sub>H<sub>12</sub>; M = C<sub>4</sub>ACH<sub>12</sub>. References: H. F. W. Taylor, The Chemistry of Cements, Vol 2, pp 394-396; cards 3-125, 4-713, Joint Committee on Powder Diffraction Standards; M. H. Roberts, Calcium Aluminate Hydrates and Related Basic Salt Solid Solutions, 5th Int Symposium on the Chemistry of Cements, Tokyo, 1968, Vol 2, 106.

Table 19. Sample 41: Ettringite.

Laboratory 3			Laboratory 6		
d, Å	I		d, Å	I	
10.72	2	Cu K <sub>α</sub> of 9.75	11.0	2	
9.75	100		9.8	10	
8.84	9		8.9	4	
7.19	1	Not ettringite	7.2	2	
5.79**	4		5.81	3	
5.62	50		5.63	8	
4.97	12		4.99	5	
4.86	4		4.86	2	
4.70	18		4.72	8	
4.43	<1				
4.02	4		4.03	3	
3.87	28		3.89	9	
3.67	3		3.68	2	
3.60	7		3.61	5	
3.48	17		3.48	7	
3.271	4		3.27	3	
3.241	12		3.24	5	
			3.20	1	
3.108**	<1		3.10	1	
3.019	4		3.02	5	
2.806	3		2.81	2	
2.774	21		2.78	9	
2.717	1		2.72	1	
			2.69	2	
2.688	6		2.68	3	
2.612	11		2.62	5	
2.562	18		2.57	9	
2.522	2		2.52	2	
2.485	2		2.49	3	
2.409	5		2.41	4	
2.348	2		2.35	4	
			2.32	1	
			2.28	1	
2.229	4		2.23	4	
2.184	4		2.21	9	
2.151	11		2.18	3	
			2.15	7	
			2.13	1	
2.123	3		2.12	2	
2.079	<1		2.08	2	
2.058	2		2.06	3	
2.030	<1				
			2.01	2	
2.003	<1				
1.976	1		1.98	2	
1.973	1				
1.943	6		1.95	4	
			1.93	1	
			1.91	2	
			1.90	1	
1.901	<1		1.87	1	
1.872	<1		1.86	4	
			1.85	2	
1.852	5				
1.843	5		1.83	2	
			1.81	2	
1.825	3		1.80	2	
1.809	1				
1.802	1		1.79	3	
1.788	<1		1.78	1	
			1.76	3	
1.765	2				
			1.75	1	
1.742	<1		1.72	2	
			1.71	4	
1.691	<1		1.68	4	
1.661	2		1.66	5	
1.634	1		1.62	4	
			1.61	1	
			1.60	2	
1.589	2				
			1.58	2	
			1.575	4	
			1.57	1	
1.558	<1				
1.540	<1		1.54	1	
			1.53	1	
			1.52	1	
			1.51	3	
1.503	<1		1.495	1	
1.491	<1		1.49	1	

\* Intensity expressed as net peak height referred to net peak height of 9.75 Å line.  
 \*\* Not on card 9-414 of Joint Committee Powder Diffraction File

logarithmic rate meter operation and full-scale chart deflection of 4000 counts per second. Radiation was nickel-filtered copper.

(3) Use of a diffractometer with an 0.006 in. receiving slit (about  $0.08^\circ$ ) and a  $1^\circ$  divergence slit (from 20 to 60 two-theta) or an  $0.5^\circ$  divergence slit (from 8 to 20 two-theta) at a scanning speed of  $0.125^\circ$  per minute with linear rate meter operation and full-scale chart deflection of 100 counts per second. Radiation was monochromated copper.

Both diffractometer techniques are suitable for use on samples producing broad peaks and both yield a small theoretical relative statistical deviation.<sup>19</sup>

### Problems in Identification of Paste Constituents

Several kinds of problems complicate the X-ray diffraction investigation of portland cement pastes. The diffraction pattern of unhydrated portland cement is itself complex, and many of the peaks are contributed to by more than one constituent. Many of the spacings of unhydrated cement persist in the hydrated pastes, particularly those of low water-cement ratio, although they diminish with the progress of hydration. A number of spacings of hydration products superpose upon spacings of unhydrated cement or upon spacings of other hydration products. An important constituent of pastes, C-S-H gel, is almost amorphous and produces broad, weak inconspicuous spacings. The platy hexagonal hydrated calcium aluminates, with and without additional anionic groups, have some spacings in common, because they have similar crystal structures and have structural units in which  $a_0$  is of the order of  $5.73 \text{ \AA} \pm 0.03$ . They can be distinguished by measuring the longest spacing accurately but this is not simple. In the first place, these long spacings lie in the region of lower diffraction angles where errors in spacing due to errors in measurement of two-theta are larger.<sup>20</sup> In the second place, a number of these substances are susceptible to carbonation and dehydration in ambient conditions found in laboratories that participated in this program, and the resulting changes have led to many anomalies and disagreements in the literature.<sup>13, 14, 15, 21, 22</sup>

The discussion in the preceding paragraph suggests that substantial improvements in the state of the art of examining cement pastes (and paste concentrates from concretes) require control of the temperature, relative humidity, and nature of the atmosphere in which the samples are prepared for X-ray diffraction and in which the examination is conducted. Kanro, Copeland, and Anderson<sup>10</sup> and Copeland, Kanro, and Verbeck<sup>23</sup> described procedures for achieving such control; Jones and Roberts<sup>24</sup> described precautions taken in work with calcium aluminate hydrates which they noted were not always satisfactory in results. Seligmann and Greening<sup>15</sup> discussed additional control measures; Dosch<sup>25</sup> has described sophisticated apparatus; many diffractometers have been equipped with shop-made chambers that permit atmosphere control of some sort in laboratories where clays are examined. Even relatively simple control methods that permit maintaining a high humidity nitrogen atmosphere in a chamber surrounding the diffraction sample will greatly improve reproducibility in the examination of atmosphere-sensitive materials. However, the anomalies reported with respect to water content and basal spacing of many of the substances are still subject to disagreement.<sup>14, 22</sup>

### Identification of Platy Hexagonal Hydrated Calcium Aluminate with and Without Additional Anions

A considerable list of these substances can be made in which  $a_0$  is about  $5.73 \text{ \AA}$  and  $c_0$  varies widely;  $c_0$  varies with water content, but  $a_0$  apparently does not.<sup>22, 26</sup> Mixed<sup>0</sup> crystals containing iron as well as aluminum can be formed in the  $C_4(A,F)H_x$  and  $C_4(A,F)\overline{SH}_x$  groups at least, and are not likely to be distinguished by X-ray diffraction from the unsubstituted forms. The ultimate products of cement hydration are believed to be substituted C-S-H gel, low-sulfate calcium sulfoaluminoferrite hydrate, the lowest sulfate form of calcium sulfohydroxyaluminate hydrate, aluminosilicate hydrogarnet, and calcium hydroxide, except that in cements of relatively low  $C_3A$  content, ettringite and unhydrated calcium aluminoferrite solid solution may be present.<sup>27</sup> However, other products have been found in early hydration stages of mixtures simulating pastes.<sup>27, 28</sup>

A list of the platy hexagonal hydrates which are thought to exist in cement pastes or mixtures like cement pastes is given below. Polytypes are not distinguished;  $C_2AH_8$ ,  $C_4A(Cl_2)H_{10}$ , and  $C_2ASH_8$  (gehlenite hydrate are omitted.)

Composition	Basal Spacing (0001)		Second Order of Basal Spacing		Low Order Spacing (hK.O)	
	d, A	I	d, A	I	d, A	I
$C_4AH_{19}$	10.6	vvs	5.32	w	2.88	s
$C_4AH_{13}$	7.92	vvs	3.95	m	2.88	s, 2.86 vs
$C_4\overline{ACH}_{11}$	7.60	vvs	3.80	ms	2.86	m
$C_4\overline{AC}O_{.5}H_{12}$	8.20	vvs	4.11	mw	2.88	vs
$C_4\overline{AC}O_{.5}H_{9-10}$	7.77	vvs	3.88	s	2.88	vs
$C_4\overline{ASH}_{14-16}$	9.6		4.80		2.87?	vs
$C_4\overline{ASH}_{12}$	8.96	vvs	4.46	s	2.87	vs
$C_4\overline{ASH}_{10}$	8.20	vvs	4.10	s	2.87	vs
$C_4\overline{ASH}_8$	$\sim 8.0$ (8.05-7.95)		$\sim 4.0$		?	

Most of these have a moderate to very strong spacing at 1.66 A. As noted earlier, the long spacings fall in the range where errors in d due to errors in measuring two-theta can be large. There are however means of increasing one's confidence that measurements in this region are adequately accurate. When ettringite is present and detectable, its spacings at 9.73 and 5.61 A are usually recognizable; if they are consistently read as  $9.73 \pm 0.02$  and  $5.61 \pm 0.02$  the spacings in between those two may be believed as read. If the sample being examined is a powder, it can be front-loaded and packed hard in the hope that preferred orientation of the platy hexagonal hydrates will be achieved and the second order of the basal spacing, which falls in a region in which spacings are less influenced by small errors in two-theta, will be accentuated. Some spacings and combinations are likely to remain ambiguous; these include the pair 7.92 and 7.77 (if it is possible to raise the humidity far enough, 7.92 should go to 10.6; 7.77 should go to 8.20 but no farther), the pair 7.77 and 7.60 (7.77 should go to 8.20 with increasing humidity but 7.60 should not change), and 8.20 (if it is  $C_4\overline{ASH}_{10}$  it will go to 8.96, but if it is  $C_4\overline{AC}O_{.5}H_{12}$  it will not). Without the ability to control and change the humidity around the sample it will be extremely difficult to establish the presence of  $C_4\overline{AH}_{13}$  as distinguished from  $C_4\overline{AC}O_{.5}H_{9-10}$  (or  $C_4\overline{ASH}_8$  which is not likely to form except in pastes dried at elevated temperature or over  $P_{2O_5}$ ) or to interpret a line at 8.2 A.

### Conclusion

X-ray diffraction permits the identification of many substances in cement paste. These include ettringite, calcium hydroxide, hydrogarnet, C-S-H gel, tetracalcium aluminate carbonate-11-hydrate and substances in residual unhydrated cement such as calcium aluminoferrite solid solutions, MgO, and residual silicates (but see (28)). If the humidity of the room is high enough or the atmosphere around the sample can be controlled, tetracalcium aluminate sulfate-12-hydrate can also be identified (or the sulfate-hydroxide solid solutions). Direct determination of  $C_4\overline{AH}_{13}$  in pastes requires control of the humidity around the sample because it can easily be confused with other possible constituents.

All those who participated in this program are indebted for a valuable educational experience to George Kalousek, who suggested and planned it, to those who prepared the pastes, and to H. A. Berman, S. Brunauer, and N. R. Greening who provided synthetic preparations and hydrated phases.

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#### DIFFERENTIAL THERMAL ANALYSIS TESTS OF HYDRATED CEMENTS AND INDIVIDUAL HYDRATES

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#### Abstract

Samples were examined in five laboratories using four different makes of equipment. Variations were observed among different analyzers. The results obtained on a given instrument were reproducible and generally suitable, within capabilities of the instrument, for at least partial analyses of the cement paste for hydrous phases. Trends of phase changes, as related to the time of curing, were the same for all laboratories. These phase changes related to the kind of cement and the water content of the paste. High instrument sensitivity (chart deflection per unit temperature difference between sample and reference) was required for optimum results.

The phases in a hydrating cement at room temperature, detected by DTA, are gypsum, calcium sulfate hemihydrate, ettringite, tetracalcium aluminate monosulfate-12-hydrate, tetracalcium aluminate hydrate, tricalcium aluminate-6-hydrate (and other hydrogarnets), calcium hydroxide, magnesium hydroxide, and substituted calcium silicate hydrate gel (C-S-H gel). The carboaluminates, in the presence of some of the above phases, are not distinctly detectable.

#### Introduction

In theory, differential thermal analysis (DTA) appears uniquely suitable for identifying or characterizing phases in hydrated cements. The anhydrous phases of the cement react with water to form hydrates which, during subsequent dehydration at constant rate of heating, absorb heat from the surroundings in reproducible amounts and at relatively definite temperatures. Also, certain exothermic reactions occur. The thermal changes (described by the terms "endothermic" for absorption of heat, and "exothermic" for evolution of heat) are the "fingerprints" for identification. Reduction of theory to practice has been relatively slow in the field of cement research.

One problem, limiting applicability of DTA, is the overlapping of endotherms of different hydrates. A more serious difficulty, which is being overcome in today's design of the instrument, has been inadequate sensitivity (chart deflection per unit temperature difference). Some of the hydrates occur in relatively small amounts in the cement pastes and often escape detection owing to lack of instrument responsiveness. A third problem relates to drying or conditioning of the samples for test. If underdried, the samples contain either free or loosely adsorbed water, which causes interference in the identification at the lower temperatures of dehydration. On the other hand, overdrying, such as heating at 100° C dehydrates partially or totally some of the phases in the cement paste. There is no absolute test for establishing the proper degree of drying. The method followed in this study is described in detail and reasons are given

for its choice.

The present program was conducted to ascertain the advantages and limitations of DTA in studying hydrated cements. As mentioned, representative results from five laboratories will be presented and are interpreted.

### DTA Equipment

The sensing element of a differential thermal analyzer is a two-junction, oppositely connected, thermocouple. One junction rests in a thermally inert material, usually ignited  $Al_2O_3$ , and the other in the sample under test. As a thermal change occurs in the sample, the emf developed in the junction of the thermocouple passes through amplification circuits and is recorded automatically on an appropriate chart. The thermal changes occur over a temperature range, often about  $100^\circ$  to  $200^\circ$  C. During this interval, the block, containing the sample and the inert material in two separate cells, is being heated at some predetermined rate. If the heat flow to the junction in the sample and that in the reference were identical, in absence of thermal reactions, there would be no unbalance between the two junctions. Under these conditions, the recorder would record only a straight line. Such a line, whether straight or with deviations (which is usually the case), is generally called the base line. The thermal change of the sample as recorded on the chart is the output of the junction of the couple relative to the base line.

The emf output of the thermocouple is obviously the summation of several factors relative to heat flow to and from the parts of the entire system, cell block, sample, etc. The specific factors affecting the recorded emf are size of sample, degree of compaction of sample, kind and size of thermocouple wire, size of welded junction (bead), material, design and size of cell block, location of thermocouple within the sample, rate of heating the cell block, immediate environment of sample during test, such as vapor pressure within sample, and kind of gaseous atmosphere, and others. Separate from these, but also affecting sensitivity, is the purely electrical amplification of the temperature couple emf.

Obviously, for a given instrument, several of these factors are constant. On the other hand, results of tests on a given sample by different instruments will show significant variations. The results of this program represent specific examples.

In Table I are given descriptions of the DTA equipment used by the five participants.

### Procedure of Conditioning Samples

As mentioned, a sample for test must not be overdried because of danger of dehydration, or partial dehydration, of some of the hydrates. Insufficient drying of the sample, on the other hand, results in the presence of free or loosely adsorbed water. Such water accentuates the endotherms at the lower temperatures and vitiates any attempt at quantitative estimates of the relative amounts of the hydrates which dehydrate at the low temperatures.

The drying of the present samples was based on some previous unreported observations that drying at a vacuum of about 0.1 mm Hg did not appear to alter any of the hydration products normally occurring at 50 percent RH and in absence of  $CO_2$ , and yet appeared to remove free water. The endpoint of drying was predetermined by drying samples for various periods of time and testing these by DTA for free water. So long as a "peak" or even an inflection persisted at a temperature of about  $110^\circ$  to  $120^\circ$  C, the presence of free or loosely adsorbed water was indicated and the sample was considered incompletely dried. The sample, if dried to the stage of absence of the  $110^\circ$  to  $120^\circ$  C peak or inflection, gave reproducible results even after substantial "overdrying" (up to 24 hr was tried) at the stated vacuum. Drying to this extent, however, does not insure completely reproducible results on such sample after dry storage for prolonged periods. The decrease in area of the C-S-H gel endotherm during dry storage is reported elsewhere (1). Other effects of dry storage of carefully prepared samples will be discussed later in this report. Such alterations during dry storage interfere with identification of the hydrous phases and unquestionably are the reason why certain apparent contradictions from highly competent experimenters have found their way into the technical literature. For reproducible results, samples should be tested as soon after preparation as possible.

### Results

The DTA data were supplied from five laboratories. It would be impractical, and actually

is not required, to present all results. The presentation is given in three steps: first, a complete series of DTA tracings for one series of cement pastes; second, results from different laboratories on individual hydrates; and, finally, comparison of results on representative samples from different laboratories.

The complete DTA tracings in Figure 1 from Laboratory 2 are for Cement 1 pastes with w/c ratio of 0.65 and cured for 1 to 365 days. The results were obtained at instrument sensitivities of 10 percent (250  $\mu\text{v}/\text{in.}$ ) from 25° to 200° C, 50 percent (50  $\mu\text{v}/\text{in.}$ ) from 175° to 500° C, 10 percent from 500° to 600° C, and 100 percent (25  $\mu\text{v}/\text{in.}$ ) from 600° to 900° C. These variations in sensitivities were required to obtain optimum results. Details of the procedure have been described (1). In the 100° to 200° C range, appear overlapping endotherms of the hydrated calcium silicate (C-S-H gel) and ettringite ( $\text{C}_6\text{AS}_3\text{H}_{32}$ ). The 1-day hydrate shows a relatively large endotherm for ettringite at 160° C and a relatively small one for gel. The latter endotherm is overlapped by the ettringite endotherm. To the experienced operator, this result means a large amount of ettringite. A procedure for separating the ettringite and C-S-H gel endotherms, with stated limitations, has been described (1). After 7 and 28 days of hydration, the amount of ettringite decreased and the amount of gel increased. At 90 days, presence of ettringite is doubtful; and, at 365 days, this phase was considered to be absent.

In the 175° to 350° C range, tetracalcium aluminate hydrate ( $\text{C}_4\text{AH}_{13}$ ) and calcium aluminate monosulfate hydrate or solid solutions of the two phases are indicated. The  $\text{C}_4\text{AH}_{13}$  (actually  $\text{C}_4\text{AH}_{19}$  prior to drying) is indicated by the endotherm at 220° C. However, as will become apparent, this endotherm overlaps one of the endotherms of the monosulfate (or solid solution), and only a rough estimation of the amount of  $\text{C}_4\text{AH}_{13}$  is possible.

The monosulfate exhibits an intricate series of endotherms, some of which can be detected only at high sensitivity of the instrument. Because the formation of the monosulfate, its subsequent transformation to the solid solution and, in turn the latter to gel, are a highly pertinent area of cement hydration chemistry, special attention is directed to this phase and its alteration products.

In Figure 2 are presented DTA curves, Nos. 1, 2, and 3 of the monosulfate and No. 4 of a solid solution of 0.75  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio at 10 percent sensitivity. Sample No. 1 was the sample distributed to all participants and was of high purity. Sample No. 2 was supplied by the Building Research Station and Sample No. 3 by the National Bureau of Standards in preliminary explorations in the program. Both samples had been in storage for some time, not recorded, but approximately two to four years at time of test. The monosulfate endotherms, excluding instrument variations, were identical for these two samples. In comparing the relatively fresh sample, No. 1, with the old samples, No. 2 or No. 3, attention is directed to the individual endotherms numbered 1 through 8. Endotherms Nos. 4 through 7 are of greatest use in depicting differences among different preparations of this phase. The large difference between Samples No. 1 and 2, or 3 is the small extent of Endotherm No. 5 and large extent of No. 6 in Sample No. 1 compared to that in No. 2 or No. 3.

In Sample No. 4, the 0.75  $\text{SO}_3/\text{Al}_2\text{O}_3$  solid solution, Endotherm No. 7 is largely missing and Endotherms No. 5 and 6 predominate. In this connection, the DTA tracing of a 20-year hydrate of Cement 18 in the Long-Time Study (LTS) program is of interest and is given in Figure 3, Curve 3. As indicated by the numbers, the solid solution in this sample exhibits a full spectrum of endotherms, with No. 7 largely suppressed and Nos. 5 and 6 similar to those of the 0.75  $\text{SO}_3/\text{Al}_2\text{O}_3$  solid solution. Thus, it is tentatively submitted (and will require further investigation) that in hydrated cements, if Endotherm No. 6 is large, and No. 7 is small, the sulfoaluminate is the solid solution.

Laboratories No. 4 and 7 also submitted DTA results on the individual hydrates. In Figure 4 (Laboratory No. 4), Curve No. 1 is that for the monosulfate used in the program and diluted in ratio of 1:5 with an inert material (presumably ignited  $\text{Al}_2\text{O}_3$ ). The curve appears different from Curve No. 1 in Figure 2, largely because of lack of fine detail resulting from low sensitivity. Also, the 230° C endotherm is disproportionately more extensive than that of No. 1 in Figure 2. In Figure 5 (Laboratory No. 7), Curve No. 1, that of the monosulfate, exhibits a single large endotherm for Peaks No. 5, 6, and 7 of the monosulfate; otherwise, Laboratory No. 7 obtained relatively good resolution of the other endotherms of the monosulfate. Laboratory No. 1 obtained nearly an identical result although using the same make of instrument as Laboratory No. 2. No satisfactory explanation could be found for this difference.

Curves for the monocarboaluminate (No. 5) and hemicarboaluminate (No. 6) are given in Figure 2. In Figures 4 and 5 are presented further results on the individual hydrates. The  $\text{C}_4\text{AH}_{10.5}$  curves were not reproduced because this sample had decomposed

Table 1. Description of DTA equipment.

Laboratory No.	1	2	4	6	7
Make of Instrument:	Deltatherm	Deltatherm	Self-Assembled	Self-Assembled	Rigaku
<u>Cell Block</u>					
Material:	Inconel	Inconel	Nickel "	Fused Al <sub>2</sub> O <sub>3</sub>	BeO-Pt Liner
Cell Size:	1/4 x 7/16"	1/4 x 7/16"	3/8 x 7/16	6 x 9 mm	9 x 22 mm
Atmos:	Ambient	Ambient	Ambient	Ambient	Ambient
Block:	Round	Round	Round	Round	Round
Vertical	Vertical	Vertical	Vertical	Cube	Vertical
Samples:	4	4	3		
<u>Diff. Thermocouple</u>					
Metal:	Chr-Al	Platinel	Pt-Pt 10% Rh	Chr-Al	Pt-Pt 13% Rh
Size Wire:	No. 28	No. 28	0.008" Dia.	26 SWG	0.3 mm Dia.
Bead:	Crossweld	Crossweld	Bead	Small	--
<u>Temp. Thermocouple</u>					
Metal:	Pt-Pt13% Rh	Pt-Pt13% Rh	Pt-Pt 10% Rh	Chr-Al	Pt-Pt13% Rh
Check:	Quartz Inversion	Quartz Inversion	No	No(a)	Yes
<u>Heating of Block</u>					
Rate:	10 C/min	10 C/min	12 C/min	10 C/min	5 C/min
Monitored?	Yes	Yes	Yes	Yes	Yes
<u>Instrument Sensitivity</u>					
Ranges	5	5	5	200	6
	100% = 15 $\mu$ v/in.	100% = 25 $\mu$ v/in.	100% = 1 mV/in.		--

(a) Standardized wire frequently changed.

Figure 1. Cement with 0.65 w/c cured 1 to 365 days (Lab. No. 2).

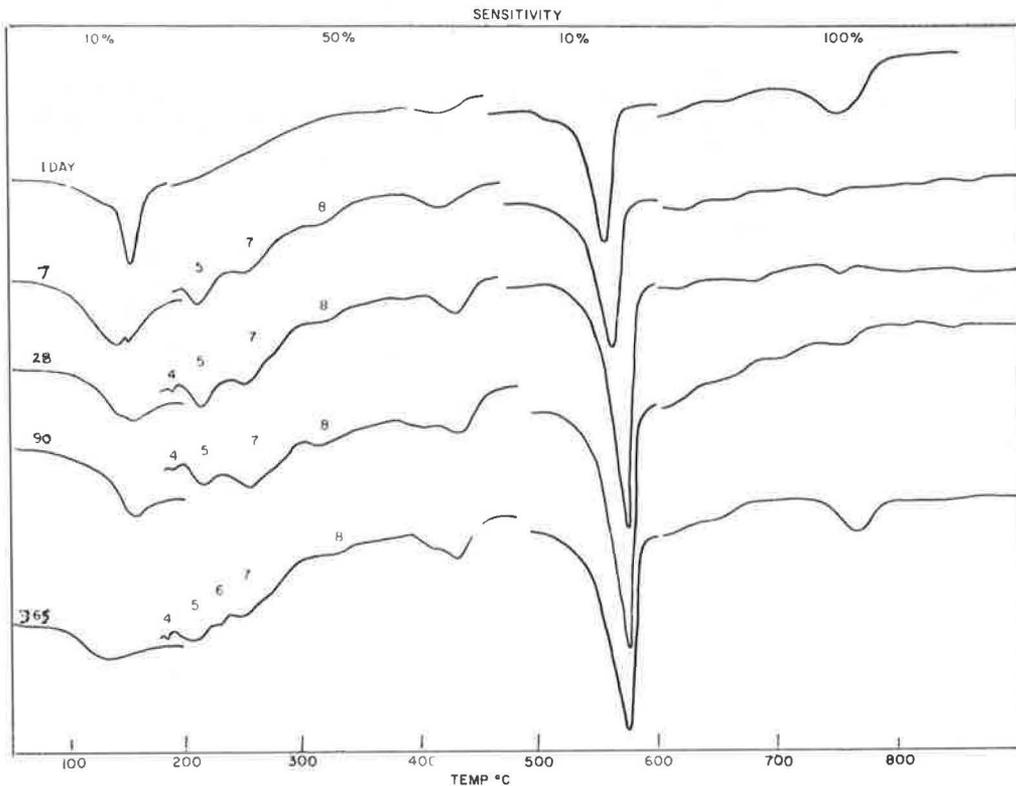


Figure 2. No. 1, monosulfate (Sample No. 39 in Program); No. 2, monosulfate from BRS; No. 3, monosulfate, old sample from NBS; No. 4, solid solution with  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio of 0.75; No. 5, monocarboaluminate (No. 38 in Program); and No. 6, hemicarboaluminate (No. 37 in the Program) (Lab. No. 2). Tests made at 10 percent sensitivity.

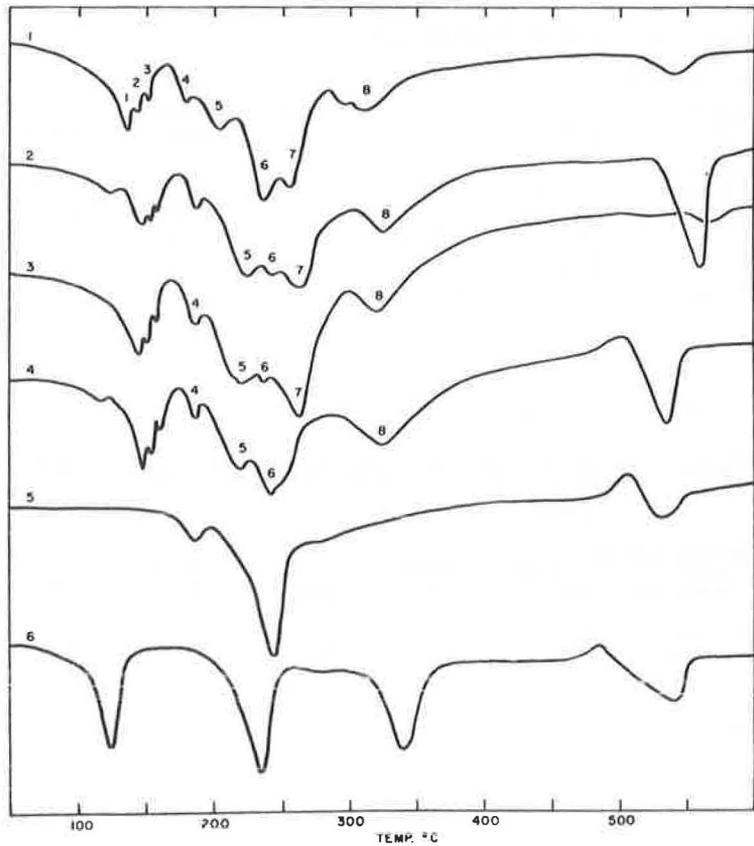
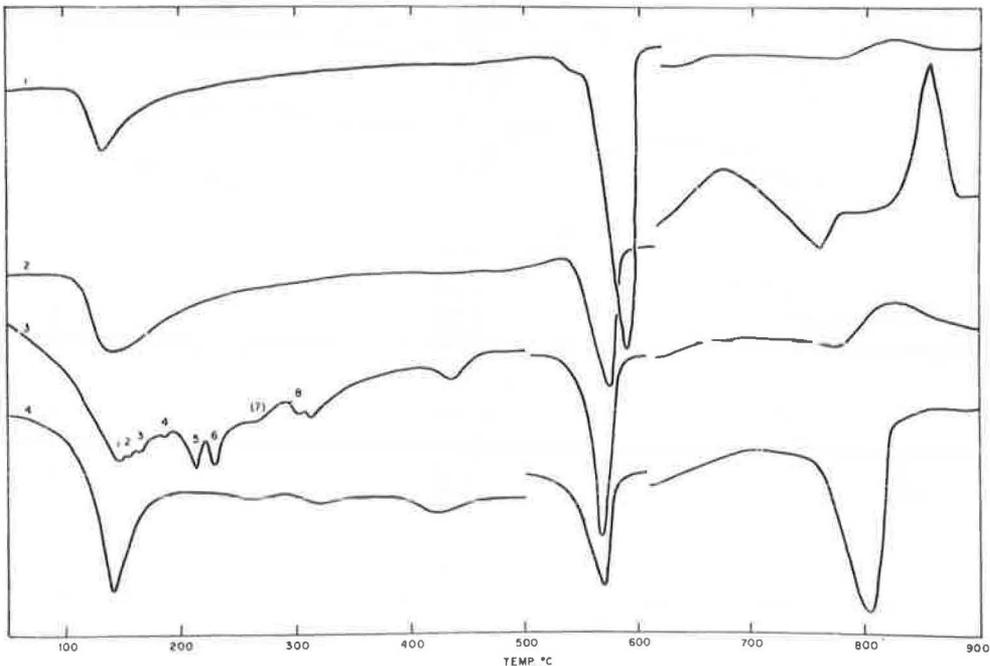


Figure 3. No. 1 is hydrated alite (Sample No. 35 in Program); No. 2 is hydrated  $\beta\text{-C}_2\text{S}$  (Sample No. 36 in Program); Nos. 3 and 4 are Long-Time Study Cements 18 and 43, respectively; hydrated for 20 years (Lab. No. 2).



extensively to  $C_3AH_6$ , and the resulting DTA curve was highly similar to that of the hemicarboaluminate shown in Figures 2 and 4, Nos. 6 and 3, respectively, except no  $CaCO_3$  was present. The hemicarboaluminate was also probably extensively decomposed to  $C_3AH_6$ . The monocarboaluminate curves, Nos. 5, 2, and 2 in Figures 2, 4, and 5, respectively, exhibit a strong endotherm at about  $205^\circ$  to  $240^\circ$ - $250^\circ$  C and other lesser endotherms.

The DTA curve for ettringite shown in two of the figures is essentially one long endotherm at about  $150^\circ$  to  $160^\circ$  C and a tendency to an endotherm at  $250^\circ$  C.

The  $C_4AH_{10.5}$  and hemicarboaluminate decomposed in dry storage.

With this background, the results in Figure 1 can be reexamined. The 1-day samples contain no monosulfate, only ettringite. The 7-day sample exhibits clearly Nos. 5, 7, and 8 endotherms; at 28 days, the extent of these increased and No. 4 was detected. Going from 28 to 90 days, the  $220^\circ$  C endotherm (No. 5), supposedly in part showing  $C_4AH_{13}$ , had decreased in size. Otherwise, the monosulfate endotherms remained essentially unchanged. Going from 90 to 365 days, the size of the endotherms decreased, indicating a decrease in amount of the monosulfate, except for Endotherm No. 6, which appeared for the first time. The monosulfate in the 365-day sample is probably better crystallized, and its better degree of crystallinity is reflected by sharper endotherms.

The increasing size in the endotherm at about  $430^\circ$  C shows the presence of  $Mg(OH)_2$  as the MgO slowly hydrates. Measurements of areas indicated that only a slight increase in the amount of  $Mg(OH)_2$  occurred between 90 and 365 days. The  $Ca(OH)_2$  endotherm increased up to age 28 days, then remained essentially constant or decreased slightly going from 90 to 365 days.

In the range of  $600^\circ$  to  $900^\circ$  C the endotherm for  $CaCO_3$ , falling approximately between  $750^\circ$  and  $800^\circ$  C, is of interest. Measurements on the 1- and 365-day hydrates of Cement 1 showed 0.45 and 0.20 percent  $CaCO_3$ , respectively, with the other three samples containing negligible amounts. Most of the samples in the program, with the 1-day hydrates of Cement 1 an exception, contained about 0.1 percent or less  $CaCO_3$  when packaged; a few contained up to 0.2 percent. It may be mentioned that the undulations in the tracings at 100 percent sensitivity reflect the cycling of the heating circuits of the instrument. (Later design of the block has largely eliminated this cycling.)

The DTA tracings (not reproduced) for the 0.35 w/c hydrates of Cement 1 in Laboratory No. 2 showed that the monosulfate had nearly completely disappeared at 90 to 365 days. The results from Laboratory No. 1, obtained on a new instrument of the same make as in Laboratory No. 2, but after nearly two years storage of the samples, showed the same general result in the 0.35 w/c samples. The No. 1 laboratory results are reproduced in Figure 6 for purposes of comparing the 0.65 and 0.35 w/c series of Cement 1. These curves were obtained at 25 percent sensitivity over the entire range; hence, in contrast to the results of Laboratory No. 2, the ettringite endotherm is much larger, and the monosulfate endotherm is much smaller. These results are presented to direct attention to changes in the monosulfate endotherms and presumably to actual change in the monosulfate during dry storage. The trend in area of the endotherms, however, was about the same for both laboratories.

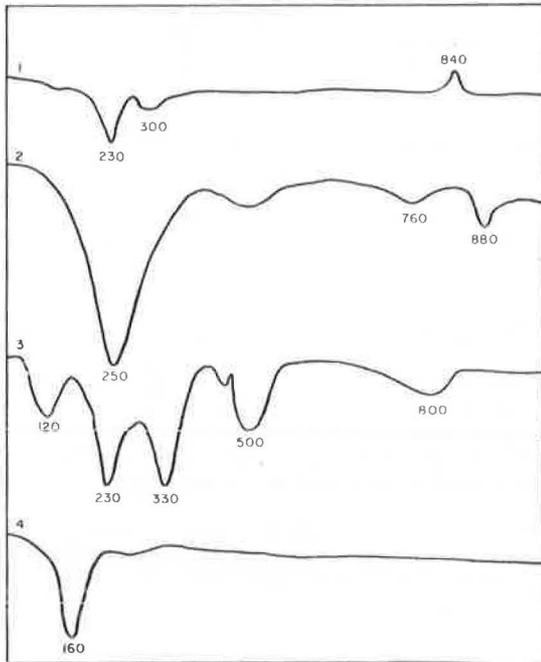
The results in Figure 6 serve to show that dried sample made from paste of low water content (0.35 w/c) follows the general transformation of ettringite  $\rightarrow$  monosulfate  $\rightarrow$  C-S-H gel (phase x (1)), and had proceeded further to completion than in pastes of the higher water content for Cement 1.

Comparisons of results from Laboratories No. 4, 6, and 7, shown in Figures 7, 8, and 9 respectively, bring out some interesting differences. These tracings, compared to those of Figures 1 and 6, of course, reflect effects of different instrumentation and different sensitivities. (Complete set of curves was not supplied by Laboratory No. 7 because of nonavailability of some of the samples. Only the results for the 0.65 w/c pastes were reproduced from Laboratory No. 4.) The 0.35 w/c samples failed to show distinguishing endotherms for the monosulfate.

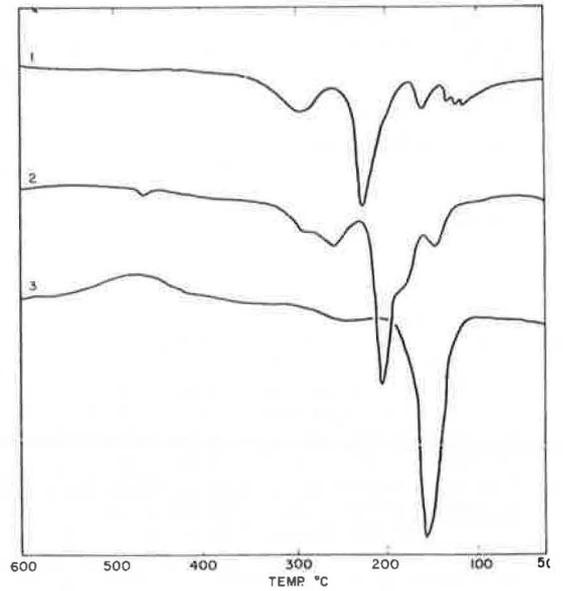
DTA results on the 0.65 w/c pastes of Cement 1 from Laboratory No. 4 are shown in Figure 7. The same general trend of changes is observed as in Laboratories No. 1 and 2, except for an apparent lower sensitivity of the instrument. The monosulfate endotherms are evident, but they lack sufficient detail to permit rigorous interpretations. The tracings from this laboratory show an exotherm at  $730^\circ$  C for some of the samples. Such an exotherm was not observed by Laboratories No. 1 and 2.

The results from Laboratory No. 6 (Figure 8) for the 0.65 and 0.35 w/c pastes of Cement 1 are in generally good agreement with those of Laboratories No. 1 and 2 except for one feature. The  $207^\circ$  C endotherm (corresponding to Endotherm No. 6) is disproportionately much larger than reported by other laboratories. Referring to Figure 2, Curves 5 and 6 for the hemicarboaluminate and monocarboaluminate, carbonation

**Figure 4. Samples used in Program tested by Lab. No. 4; No. 1 is monosulfate; No. 2 is monocarboaluminate; No. 3 is hemicarboaluminate; and No. 4 is ettringite.**



**Figure 5. Samples used in Program tested by Lab. No. 7; No. 1 is monosulfate; No. 2 is monocarboaluminate; and No. 3 is ettringite.**



**Figure 6. Cement 1 with 0.65 and 0.35 w/c cured to 1 to 365 days (Lab. No. 1).**

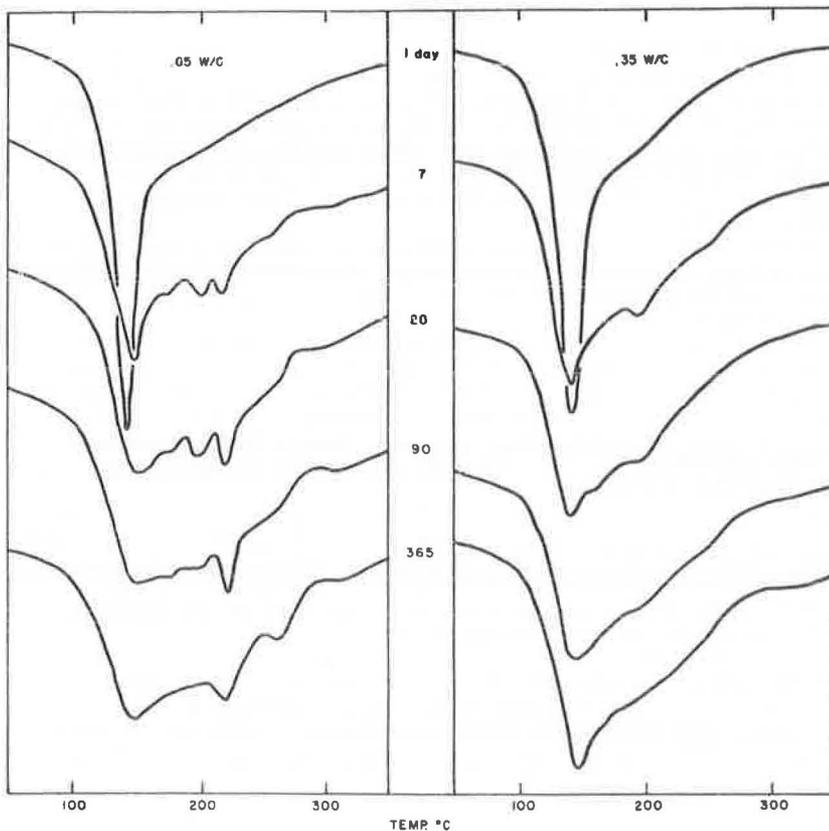


Figure 7. Cement 1 with 0.65 w/c cured 1 to 365 days (Lab. No. 4).

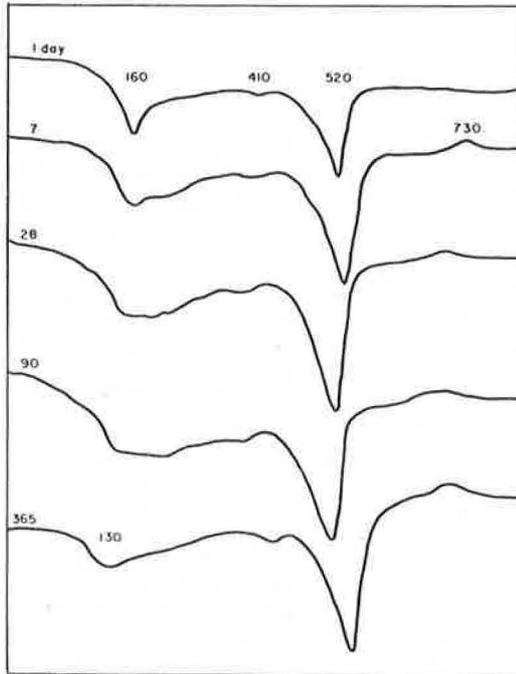
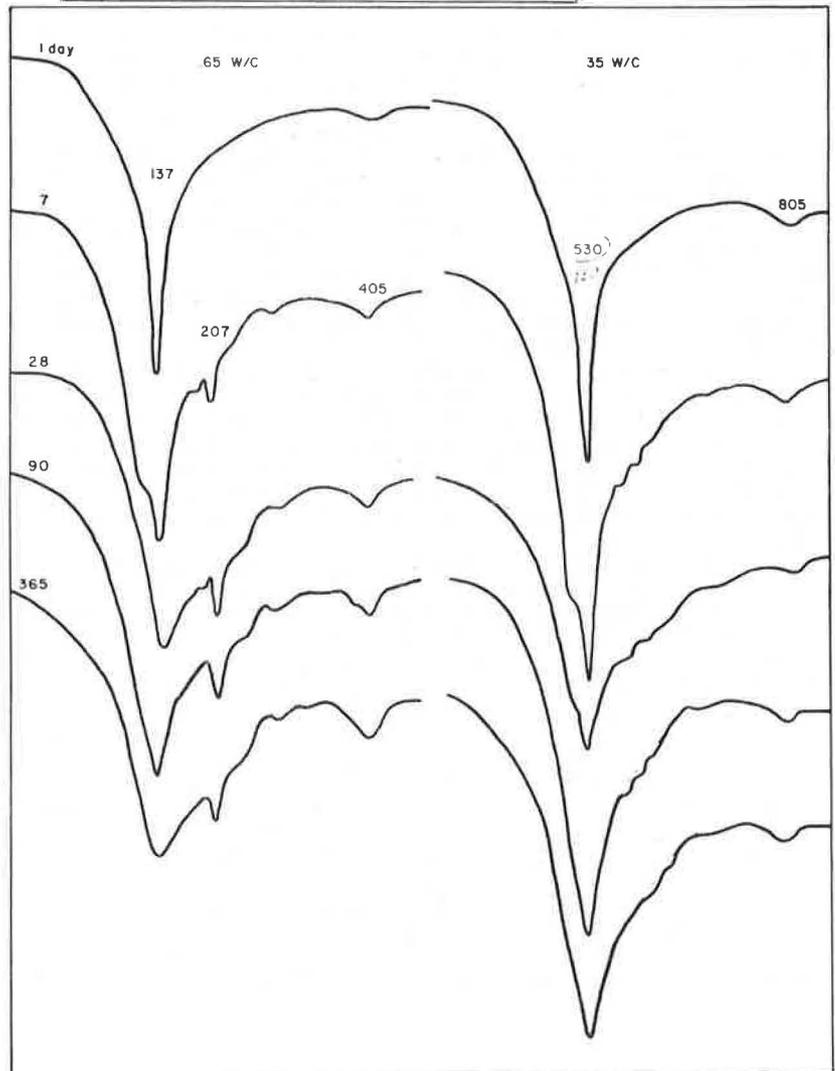


Figure 8. Cement 1 with 0.65 and 0.35 w/c cured 1 to 365 days (Lab. No. 6).



in storage would be suspect. Examination of the curves, which showed some carbonation in two samples and none in the others, precludes carbonation as an explanation. The 207° C endotherm, corresponding to Endotherm No. 6 of the monosulfate, is the endotherm associated with  $C_4AH_{13}$ . It seems improbable, however, that the monosulfate would break down into  $C_4AH_{13}$  in one laboratory and not the others. This difference may be attributed to some still unknown factors in instrumentation and techniques. It is important to note that Laboratories No. 2, 4, and 7 showed an extensive endotherm at about 220° to 230° C in the pure sample of the monosulfate, but not in the cement pastes.

The instrumentation in Laboratory No. 6, presumably with relatively high recorder speed and perhaps too high a sensitivity in the 25° to 200° C temperature range, contributes to poor or no separation of the C-S-H gel and ettringite endotherms (Figure 8).

The tracings in Figure 9 reported by Laboratory No. 7 for both the 0.65 and 0.35 w/c pastes (available for test) showed the same general trends as observed by Laboratories No. 1, 2, 4, and 6. The sensitivity of the instrument in Laboratory No. 7 was not sufficiently high to secure as complete resolution for monosulfate as in Laboratories No. 1, 2, and 6, but trends are unmistakably the same except for the size of the No. 6 endotherms in tracings from Laboratory No. 6. Laboratory No. 6 did not report DTA results for the pure monosulfate and, therefore, attention is directed to the results obtained by Laboratory No. 7 shown in Figure 5 and Laboratory No. 4 shown in Figure 4 for the monosulfate. It is seen that the No. 6 endotherm, nominally at 210° to 230° C, is relatively extensive. Laboratories No. 4 and 7 had one instrumental feature in common, platinum couples. It is not known if this is a factor accounting for the observed difference. Another thermal change occurring sporadically was an exotherm at about 750° to 830° C. This exotherm did not correlate with any known variation in sample composition or treatment.

Only a limited number of results are being presented on Cements 2 and 3 because the results from one laboratory fairly well illustrate the results obtained from other laboratories, and within the variations already noted. The DTA tracings are presented in Figure 10.

Results on Cement 2, the white cement, show clearly the formation of ettringite in abundance at 1 day for both w/c ratios. Ettringite decreased in amount between 1 and 7 days and thereafter, but more slowly, for the duration of the test up to 365 days. At 365 days, the inflection in the curve at 150° to 160° C indicates the presence of little ettringite for pastes of both w/c ratios. The amounts of monosulfate remained approximately the same for both w/c ratios between 7 and 365 days. At 365 days, the endotherms for the monosulfate were clearly defined, indicating recrystallization to larger crystals of this hydrate between 90 and 365 days. Measurements following procedures described previously (1) show that only about one-fourth of the total  $SO_3$  was combined as the monosulfate.

The difference in the effect of water content with Cements 1 and 2 may be noted. The 0.35 w/c ratio in pastes of the white cement had no apparent effect on the equilibrium: ettringite  $\rightarrow$  monosulfate  $\rightarrow$  gel, as it did in the pastes of No. 1 cement.

No. 3 cement (zero  $C_3A$ ) yielded partially hydrated phases with few distinguishing DTA characteristics. The tracings for this cement (Figure 10) contain no indication of the presence of the monosulfate and, therefore, indicate this hydrate did not form. Absence of the monosulfate in pastes of high  $C_4AF$  cements had been previously observed (2, 3, 4, 5).

The DTA curves as presented show that ettringite had formed at one day and apparently persisted through 90 days and even to 365 days. Based on the extent of the ettringite endotherm in the 24-hour paste of Cement 3 compared to the extent of this endotherm of 24-hour pastes of Cements 1 and 2, it appears that much less ettringite is present in the paste of Cement 3. Gypsum was not detected. It may be assumed, therefore, that even during the first 24 hours of hydration, some of the  $SO_3$  had combined with the hydrating calcium silicate to form phase X (C-S-H gel).

The inability to separate phase X and ettringite endotherms may leave the impression from a casual examination of the areas of the 100° to 200° C endotherm that ettringite persists in about equal volume going from 1 to 90 days or even, perhaps, to 1 year. In interpreting these test results, it has to be recognized that the phase X endotherm increased steadily in area and tended to "bottom" out at a lower temperature, 130° C with increasing age of curing, and that the endotherm of the  $Fe_2O_3$ -bearing ettringite tends to overlap the C-S-H gel endotherm more than for other cements. This splitting of the 100° to 200° C endotherm is apparent only for the 0.65 w/c sample cured for 365 days. Ettringite is still present at 365 days, but in substantially reduced amount.

Continued hydration of present samples would be expected to culminate in complete elimination, or reduction to a small amount, of ettringite. The results on a high  $C_4AF$

Figure 9. Cement 1 with 0.65 and 0.35 w/c cured 28 to 365 days (Lab. No. 7).

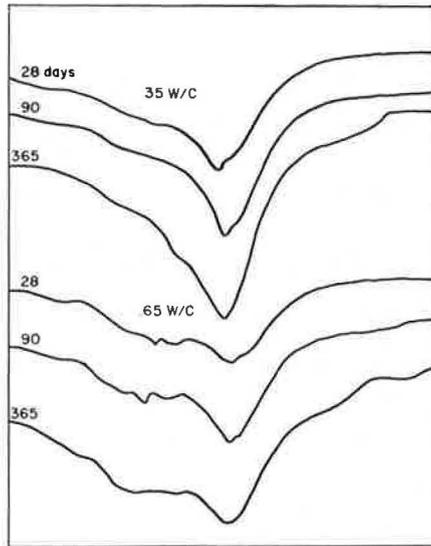
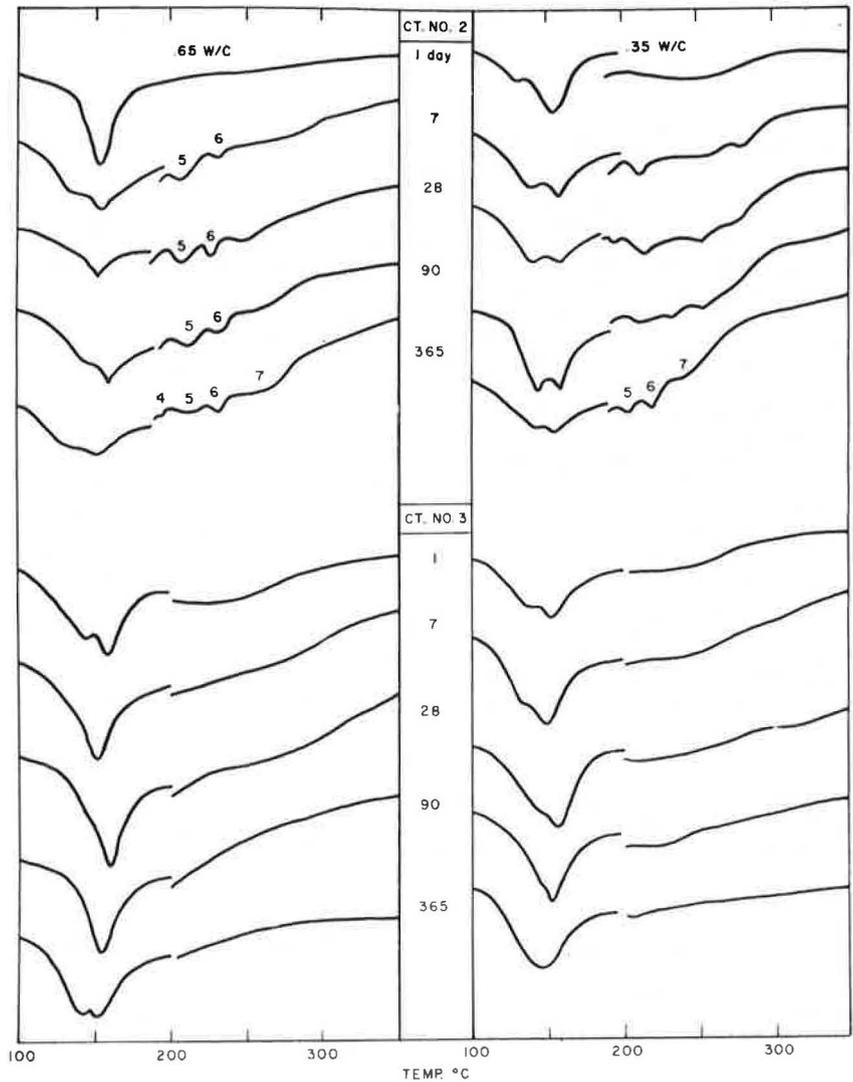


Figure 10. Cements 2 and 3 with 0.65 and 0.35 w/c cured 1 to 365 days (Lab. No. 2).



cement paste (LTS 43) after 20-year period of hydration are shown in Figure 3, Curve 4. The endotherm, at 50 percent sensitivity, falls at 130° C and ettringite was not present, or was in small amount only, probably 0.5 percent or less, as suggested by examinations of blends of cement paste and known amounts of ettringite. It is interesting to note that the 20-year hydrate of Cement 43 does not contain any monosulfate or solid solution. The extended endotherm at 310° C shows the presence of a little hydrogarnet (perhaps about 1 to 2 percent).

In Figure 3 are presented the complete DTA tracings obtained in Laboratory No. 2 on alite (No. 1) and  $\beta\text{C}_2\text{S}$  (No. 2) hydrated at room temperature for over 5 years. These two samples were tested at 10 percent sensitivity to 625° C, then at 100 percent to 900° C. Two distinct differences are apparent between these two C-S-H gels, exclusive of the larger amount of  $\text{Ca}(\text{OH})_2$  from the alite which, of course, is expected. The gel endotherm for the hydrated alite is relatively sharp and occurs at 130° C at the exact temperature at which it occurs for phase X. The endotherm for hydrated  $\beta\text{-C}_2\text{S}$  is rounded and the "peak" occurs at about 150° C. Hydrated alite shows no thermal changes in the 600° to 900° C range, whereas hydrated  $\beta\text{C}_2\text{S}$  shows an exotherm at 860° C of relatively small extent when allowance is made for the 100 percent sensitivity of the instrument. DTA also shows that a little of the  $\text{Ca}(\text{OH})_2$  of the hydrated alite dehydrates at lower temperature than the major portion. Such dehydration at the lower temperature may be attributed to finely subdivided  $\text{Ca}(\text{OH})_2$ . It may be assumed that some of the  $\text{Ca}(\text{OH})_2$ , probably embedded in the gel does not recrystallize even on prolonged standing. The exotherm at 860° C has been associated with C-S-H gel of lower  $\text{CaO}/\text{SiO}_2$  ratio. It is uncertain what the composition of this phase might be because of the unknown effect of the  $\text{B}_2\text{O}_3$  used to stabilize the  $\beta\text{C}_2\text{S}$  during preparation of the anhydrous phase.

#### Summary and Discussions

1. The DTA results varied significantly among different makes of instruments. The factors which affect the thermocouple output as a tracing on the charts were discussed. Many of these are instrument constants and cause no variation from test to test on a given instrument.

2. The important variable requiring control for optimum DTA results is the overall sensitivity of the instrument--the emf output of the thermocouple for a given temperature difference combined with the controlled amplification of the signal. There are limitations on the degree of amplification, owing to background "noises," abnormal drifting of the base line, and other factors. An instrument's capability to yield optimum results, particularly for detecting small amounts of some of the phases, depends on the stability of the emf output at high amplification.

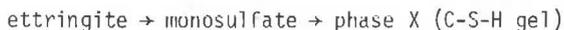
Although not studied as such, the rate of heating and the chart speed are important factors in separating overlapping endotherms such as those for ettringite and C-S-H gel.

3. DTA tests of pastes of high  $\text{C}_4\text{AF}$  cement require auxiliary tests on blends of an extensively hydrated paste and ettringite. The endotherm of gel and the  $\text{Fe}_2\text{O}_3$ -bearing ettringite tend to overlap more closely than those of other cement pastes. Additions of known amounts of ettringite to such pastes and examination with DTA are helpful for interpretations regarding presence of ettringite. Even this procedure is not critically decisive in detecting presence of small amounts of ettringite.

The monosulfate was not detected in any paste samples of the high  $\text{C}_4\text{AF}$  cement.

4. In the pastes of "average" Type I cement a low water content ( $w/c.35$ ) markedly reduced monosulfate formation. In pastes of white cement, reduction of water content did not have this effect on the formation of monosulfate.

5. The DTA results show that the course of the generalized reaction,



is affected by the water content of the pastes, the type of cement, and the age of curing. In pastes of cements of high  $\text{C}_4\text{AF}$  content after prolonged curing, the above reaction is largely or completely terminated in C-S-H gel.

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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).

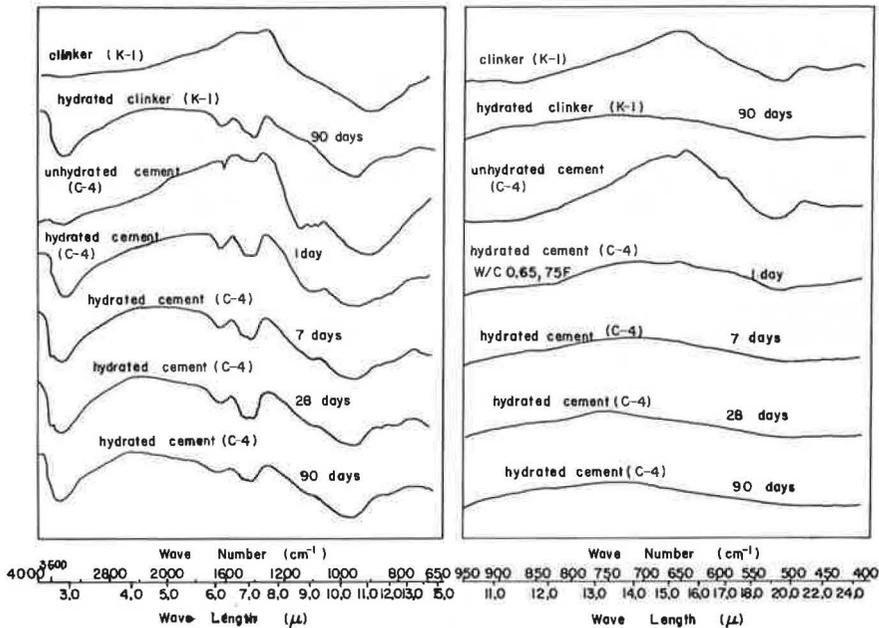


Figure 2. IR spectra of hydrated compounds (KBr).

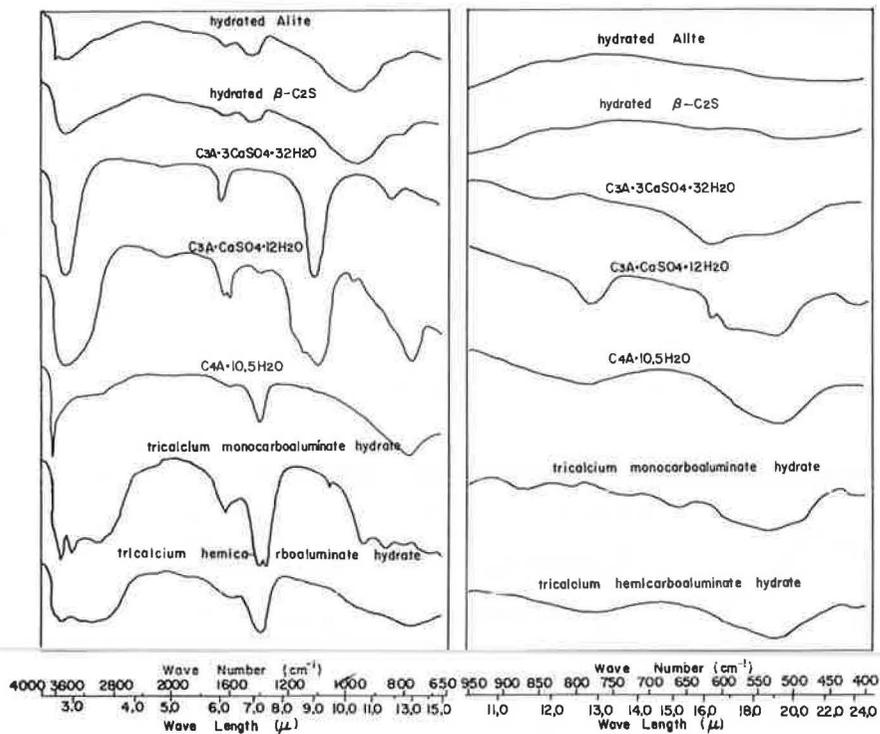


Figure 3. Absorption of SO<sub>4</sub><sup>2-</sup> ion in unhydrated and partially hydrated cement (w/c = 0.65) (KBr).

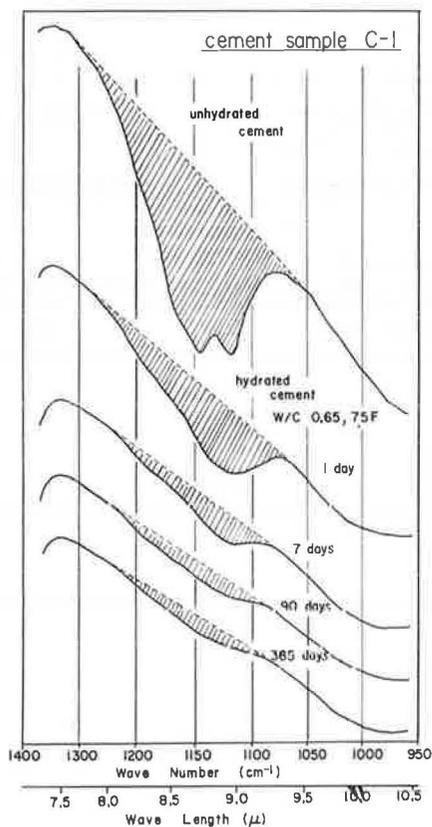


Figure 4. Relation between area of absorption of  $SO_4^{2-}$  ion in partially hydrated cement and curing period ( $w/c = 0.65$ ) (KBr).

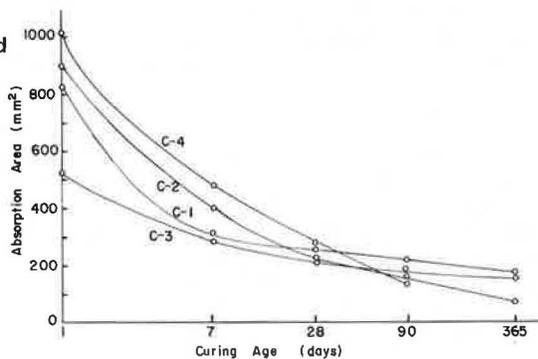
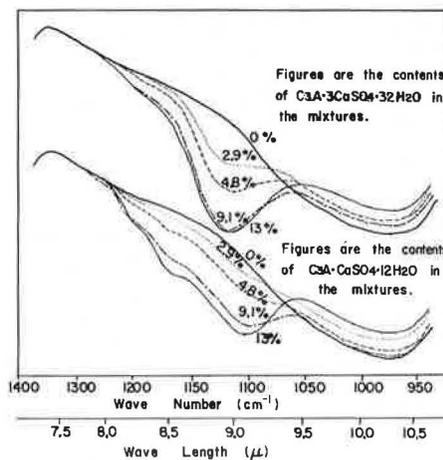


Figure 5. IR spectra of the mixtures of hydrated alite and hydrous calcium sulfoaluminate.



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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