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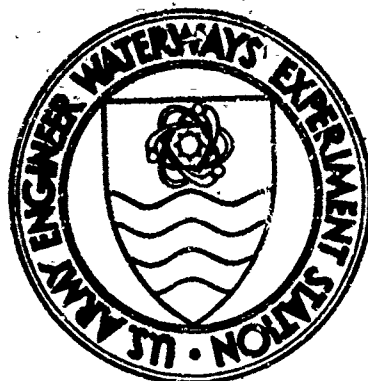
Examination of Cement Pastes Hydrated Phases, and Synthetic Products by X-Ray Diffraction

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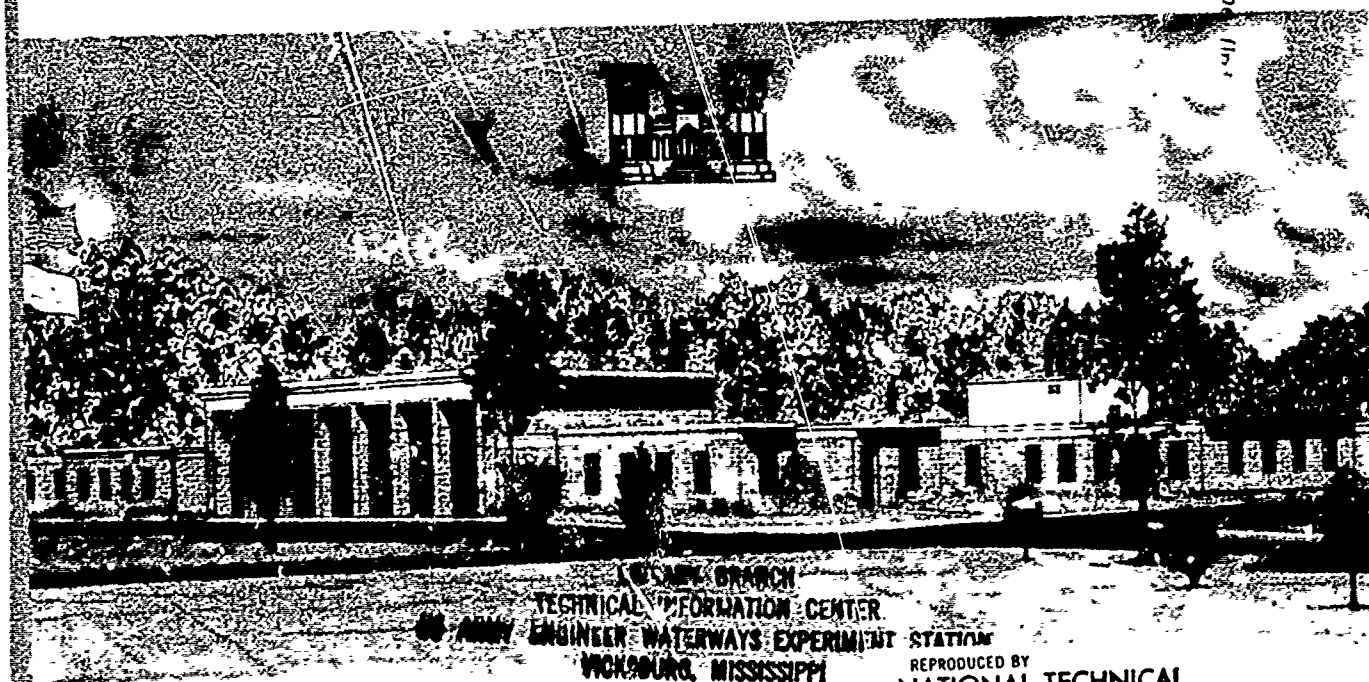
EXAMINATION OF CEMENT PASTES HYDRATED PHASES, AND SYNTHETIC PRODUCTS BY X-RAY DIFFRACTION

by

K. Mather

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Pastes of three cements were examined by X-ray diffraction at five ages in seven laboratories. Six of the laboratories used X-ray diffractometers and one used a focusing camera of the Guinier type. Six laboratories examined hydrated phases and synthesized hydrates. This is the first cooperative program in X-ray diffraction of portland cement pastes and synthetic hydrates of which we have knowledge. Pastes of all three cements were mixed at water-cement ratios of 0.35 and 0.65 and were examined after hydration had been stopped at ages of 1, 7, 28, 90, and 365 days. Pastes of a Type I cement at 0.35 water-cement ratio contained ettringite, tetracalcium aluminate monosulfate-12-hydrate, calcium hydroxide, calcium silicate hydrate gel, and residual cement constituents. Tetracalcium aluminate monosulfate-12-hydrate was detected at 7 days and increased thereafter at the expense of ettringite. Compositions of pastes of this cement at 0.65 water-cement ratio were similar to those of the pastes of 0.35 water-cement ratio; the sequences of hydrates appearing and increasing, and cement constituents diminishing and in some instances disappearing, were more conspicuous. The sequence of development and constituents present in pastes of a white cement at the two water-cement ratios resembled the Type I pastes. Pastes of a third cement containing no tricalcium aluminate formed less ettringite than pastes of the other two cements; ettringite persisted to one year; tetracalcium aluminate monosulfate-12-hydrate was detected only in trace amounts. Spacings present in hydrated alite, hydrated β-C₂S, tetracalcium aluminate hemicarboxylate-12-hydrate, tetracalcium aluminate carbonate-11-hydrate, tetracalcium aluminate monosulfate-12-hydrate, unstable tetracalcium aluminate-10.5-hydrate, and ettringite, are reported.		

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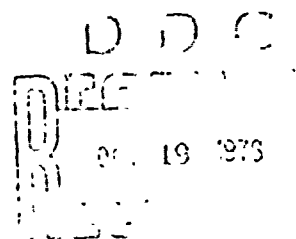
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Foreword

This report includes the results of a cooperative program on X-ray diffraction studies of cement pastes, hydrated phases, and synthetic hydrates. The work reported formed a part of a cooperative research program sponsored by the Committee on Basic Research Pertaining to Portland Cement and Concrete of the Highway Research Board. The program on evaluation of methods of identifying phases in cement pastes was initiated by Dr. George Kalousek while Dr. R. C. Mielenz was chairman of the committee, and was conducted by a task group headed by Dr. Kalousek while Dr. W. L. Dolch was chairman of the committee. Dr. Dolch became chairman of the task group in 1969.

Under the Engineer Studies Program of the Office, Chief of Engineers (ES Item 614.2) the Concrete Division of the U. S. Army Engineer Waterways Experiment Station took part in the cooperative X-ray diffraction work. The work was done under the supervision of Thomas B. Kennedy, Bryant Mather, and R. V. Tye, Jr. The X-ray diffraction was done by Wilbur I. Luke, Delbert E. Day, and Alan D. Buck. The other cooperating laboratories provided reports of their results to Katharine Mather who prepared the report as a section of the report on the whole project.

Directors of the WES while this work was going on were COL Alex G. Sutton, CE, COL John R. Oswalt, Jr., CE, COL Levi A. Brown, CE, and COL Ernest D. Peixotto, CE. Mr. Joseph B. Tiffany, Jr., and Mr. Frederick R. Brown were Technical Directors.

Contents

	<u>Page</u>
Foreword	iii
Summary	vii
Introduction	1
Participants	1
Approach	2
Samples - cement pastes	2
Samples - hydrates and synthetic products	3
Instrumentation	3
Examination of pastes	4
Results	4
Examination of hydrates and synthetic products	12
Discussion: detection of C-S-H gel	15
Problems in identification of paste constituents	16
Identification of platy hexagonal hydrated calcium aluminate with and without additional anions	18
Conclusion	20
REFERENCES	22
TABLES 1-19	
FIGURES 1-7	

Summary

Pastes of three cements were examined by X-ray diffraction at five ages in seven laboratories. Six of the laboratories used X-ray diffractometers and one used a focusing camera of the Guinier type. Six laboratories examined hydrated phases and synthesized hydrates. This is the first cooperative program in X-ray diffraction of portland cement pastes and synthetic hydrates of which we have knowledge.

Pastes of all three cements were mixed at water-cement ratios of 0.35 and 0.65 and were examined after hydration had been stopped at ages of 1, 7, 28, 90, and 365 days. Pastes of a Type I cement at 0.35 water-cement ratio contained ettringite, tetracalcium aluminate monosulfate-12-hydrate, calcium hydroxide, calcium silicate hydrate gel, and residual cement constituents. Tetracalcium aluminate monosulfate-12-hydrate was detected at 7 days and increased thereafter at the expense of ettringite. Compositions of pastes of this cement at 0.65 water-cement ratio were similar to those of the pastes of 0.35 water-cement ratio; the sequences of hydrates appearing and increasing, and cement constituents diminishing and in some instances disappearing, were more conspicuous. The sequence of development and constituents present in pastes of a white cement at the two water-cement ratios resembled the Type I pastes. Pastes of a third cement containing no tricalcium aluminate formed less ettringite than pastes of the other two cements; ettringite persisted to one year;

tetracalcium aluminate monosulfate-12-hydrate was detected only in trace amounts.

Spacings present in hydrated alite, hydrated γ -C₂S, tetracalcium aluminate hemicarborate-12-hydrate, tetracalcium aluminate carbonate-11-hydrate, tetracalcium aluminate monosulfate-12-hydrate, unstable tetracalcium aluminate-10.5-hydrate, and ettringite, are reported.

Examination of Cement Pastes, Hydrated Phases,
and Synthetic Products by X-Ray Diffraction

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,⁽¹⁾ Taylor,^(2,4) Heller and Taylor,⁽³⁾ Turriziani and colleagues,^(5,6,7) Kalousek,⁽⁸⁾ Midgley,⁽⁹⁾ Kantro, Copeland, and Anderson,⁽¹⁰⁾ 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, Garston, 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, 1071-1 Ohaza Kogushi, Ube-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 most 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_3A 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_2 , the other two 0.4 to 0.5 percent CO_2 . 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 hr at 40-50 μ 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 hard-dried powder. The results obtained were very similar to those obtained by examining the pastes originally distributed.

Samples - hydrates and synthetic products

Samples of hydrates of alite and β -C₂S, 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.⁽¹¹⁾

Instrumentation

The instruments used by the cooperating laboratories are identified in table 3. Five of the diffractometers were essentially 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 more able to detect weak lines, and thus to detect small quantities, than their diffractometer. Operating conditions reported are shown in tables 4a and 4b.

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 in different laboratories with different instrumentation.

The available hydrated alite and belite, and synthetic products offered the participants the opportunity of examining carefully prepared samples of substances that are present or may be present in mixture 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 procedure 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 none to several years experience; the expertise of the X-ray 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 of 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; others 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 10⁻¹⁰</u>	
	<u>Laboratory 3</u>	<u>Laboratory 6</u>
Ettringite	9.8	9.8
C ₄ A $\bar{S}$ H ₁₂	8.9	8.9
C ₃ A $\bar{C}$ O _{0.5} H ₁₂	8.2	8.2
C-A hydrate	-	7.9
C ₄ A $\bar{C}$ H ₁₁	7.7	7.7
Calcium hydroxide	4.90, 2.63	4.9
Hydrogarnet	5.06, 2.54	2.54
C-S-H	3.03, 1.82	3.04, 2.98
Alite	2.97, 1.76	2.79
Belite	2.88*	2.88
C ₃ A	2.69	2.69
Aluminoferite SS	7.3, 2.65	7.3, 2.66
MgO	2.10	2.10
Calcite	**	2.29

* Line interfered with by C₄A $\bar{S}$ H₁₂

** With Cement No. 1, 2.10, 2.28; with cement No. 2, 3.88, 2.23, 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.

All of the participating laboratories reported the presence of calcium hydroxide in pastes of all three cements at both water-cement ratios 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). $C_4A\bar{S}H_{12}$ 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, $C_4A\bar{S}H_{12}$ 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 $C_4A\bar{S}H_{12}$ 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⁽¹⁰⁾ reported hydrogarnet in pastes of cements of several types; it has also been reported from field concretes.⁽¹²⁾

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

Three other hydrates were reported: $C_4A\bar{C}H_{11}$, 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 29 Å

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 at 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 deg 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 the pastes 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. $C_4A\bar{S}H_{12}$ 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 Å are taken as unequivocal evidence of the presence of alite, the 5.94 Å 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 Å is recognizable but very very weak at 365 days, and the line at 1.76 Å through

365 days in the pastes of lower w/c. In the pastes of 0.65 water-cement ratio 1.76 is perceptible through 28 days but 2.97 is not. The 2.70 line of C-A is probably present at 7 days, not thereafter, in the pastes 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 can be recognized. At both water-cement ratios, MgO decreased noticeably from 1 to 7 days but did not change perceptibly thereafter. In the pastes of both water-cement ratios the 2.88 peak appeared to increase from 7 days over what it was at 1 day, showing the presence of $C_4\bar{A}SH_{12}$ and rendering the peak only dubious evidence of belite. The aluminoferrite line at 1° 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 Å increase with age. The ettringite lines are more intense in the pastes of 0.65 water-cement ratio through 90 days; $C_4\bar{A}SH_{12}$ 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 line diminishes from 1 day through 90 days and then increases at 365 in the pastes of 0.65 water-cement ratio. In the pastes of 0.35 water-cement ratio, the 2.88 line increases from 7 days, showing the increase in $C_4\bar{A}SH_{12}$ but making the spacing dubious as evidence of belite. The C_3A line at 2.70 Å 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 Å and 1.76 Å lines of alite persisted at 365 days; in the paste of higher water content, the 2.97 line was not recognized at 90 days, the 1.76 Å 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; $C_4A\bar{S}H_{12}$ could be detected in pastes cured more than 1 day but it was less conspicuous than the ettringite. The belite line at 2.88 Å 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 and 1.76 Å were detected at 365 days in the paste of lower water content; the 2.97 Å line was detected at 28 days and the 1.76 Å line was barely detected at 90 days in the paste of higher water content. Aluminoferriite lines including the weak line at 3.66 Å persisted at 365 days in pastes of both water contents.

Table 12 shows scaled intensities of characteristic peaks of ettringite, $C_4A\bar{S}H_{12}$, 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 broad lines at 3.07 and 1.82 Å (fig. 7). Laboratory 6 reported a line at 1.97 not resolved by laboratory 3 and identified it as another C-S-H gel spacing. Laboratory 3 described the spacing at 3.066 Å as a broad asymmetric hump from about 26 to 38 two-theta, rising steeply from 28 to 29.3 and then sloping gently to background at 38. The spacing at 1.812 Å 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 at about 2.80 was apparently inconspicuous.

The hydrated β -C₂S (table 14) contained less calcium hydroxide, a larger number of spacings characteristic of unhydrated β -C₂S, and the spacing at 2.67 Å (reported by three laboratories) identified by laboratory 3 as C-S-H gel, as well as spacings at 3.05 or 3.66, 2.615(?) or 2.76, and 1.81° or 1.32°, characteristic of 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.

$C_4\bar{A}\bar{C}_{0.5}H_{12}$ was examined in six laboratories; in four of these the sample contained $C_4\bar{A}\bar{C}_{0.5}H_{10}$ as well as $C_4\bar{A}\bar{C}_{0.5}H_{12}$. It also contained a small amount of $C_3\bar{A}H_6$. Dosch and zur Strassen⁽¹³⁾ obtained $C_4\bar{A}\bar{C}_{0.5}H_{12}$ with a basal spacing of 1.2 Å at 81 percent relative humidity and a dehydration product with a basal spacing of 7.7 Å and a water content

recorded as 9 H₂O at 11 percent relative humidity; it does not appear that they investigated the production of the partial dehydrated phase at higher humidities. Since the 7.7-A phase appeared in four laboratories it seems probable that dehydration of the 8.2-A phase begins at relative humidities above 11 percent. Dosch, Keller, and zur Strassen⁽¹⁴⁾ have found that the CO₃ content of the material described by Seligmann and Greening⁽¹⁵⁾ as C₃A·1/2Ca(OH)₂·1/2CaCO₃·H_x (equal to C₄A_{0.5}H_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 C₄A_{0.5}H₁₁ reported by two laboratories. Very small amounts of C₃AH₆ were reported by four of the six laboratories that examined this sample. There was no indication that any dehydration stage of C₄A_{0.5}H₁₁ was present.

Spacings of tetracalcium aluminate monosulfate-12-hydrate (C₄A_{0.5}H₁₂) recorded by two laboratories are shown in table 17. Five laboratories examined this sample; all found a very small amount of ettringite with the monosulfate. Partial dehydration of the sample occurred in three of the laboratories; in two of them 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 CaCl₂ (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 14 (H₂O)₂·6H₂O which produces a relative humidity over 90 percent at

about 23 °C (55% r.h. at 18 °C, 21.5% at 31 °C) which returned all of the sample to the 12-hydrate condition.

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

Laboratory

1	C_4AH_{13} , $C_4\bar{A}CH_{11}$; C_3AH_6 , CH
2	C_4AH_{13} ; C_3AH_6 , CH
3	$C_4\bar{A}C_{0.5}H_{12}$, C_3AH_6 , CH
5	$C_4\bar{A}C_{0.5}H_{12}$, $C_4\bar{A}C_{0.5}H_{10}$; C_3AH_6 , CH
6	$C_4\bar{A}C_{0.5}H_{12}$, 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⁽¹⁶⁾ lists spacings from 9.73 to 1.768 Å, including a total of 50. Participants in this program reported 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⁽¹⁷⁾ have described the structure of

naturally occurring ettringite from Scawt Hill. The crystal symmetry is trigonal with space group P3lc; 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 $C_4\bar{A}SH_{12}$ and $C_4\bar{A}H_{13}$ with SO_3 to Al_2O_3 as 0.75 to 1.00. The constituents recognized were $C_4\bar{A}SH_{12}$, $C_4\bar{A}SH_{10}$, and $C_4\bar{A}CH_{11}$ although the sample was examined in a chamber which had an atmosphere above 90 percent relative humidity.

D. 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 3-C₂S for 5.3 years yields broad weak spacings at about 3.05 to 3.07 Å and 1.82 Å, with the more intense at 3.05-3.07 Å asymmetric, dropping steeply toward lower diffraction angles and tailing off gently to about 38 two-theta; the third spacing at 2.6 Å reported for nearly amorphous calcium silicate hydrates by Taylor⁽¹⁸⁾ was not conspicuous in the hydrated alite (table 13, fig. 7) examined in this program and was masked in the hydrated 3-C₂S by residual unhydrated material. The cement pastes of 0.65 w/c hydrated for 1 year (fig. 7) had the 2.80-Å 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 2.6 Å 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 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°) and a 1° divergence slit (from 20 to 60 two-theta) or an 0.5° divergence slit (from 8 to 20 two-theta) at a scanning speed of 0.125° 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.⁽¹⁹⁾

Problems in identification of paste constituents

Several kinds of problems perplex the X-ray diffraction investigation of portland cement pastes. The diffraction pattern of unhydrated portland cement is in itself complex and many of the spacings are contributed to by more than one constituent. Many of these 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 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 maximized.⁽²⁰⁾ 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 that have led to many anomalies and disagreements in the literature.^{(13,14,15,21,22).}

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. Kantro, Copeland, and Anderson⁽¹⁰⁾ and Copeland, Kantro, and Verbeck⁽²³⁾ described procedures for achieving such control; Jones and Roberts⁽²⁴⁾ describe precautions taken in work with calcium aluminate hydrates which they noted were not always satisfactory in results. Seligmann and Greening⁽¹⁵⁾ discussed additional

control measures; Dosch⁽²⁵⁾ 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.^(14,22)

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 and c_0 varies widely; c_0 varies with water content but a_0 apparently does not.^(22,26) Mixed crystals containing iron as well as aluminum can be formed in the $C_4(A,F)H_x$ and $C_4(A,F)\bar{S}H_x$ 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.⁽²⁷⁾ However, other products have been found in early hydration stages of mixtures simulating pastes.^(27,28)

A list of the platy hexagonal hydrates which may be thought to exist in cement pastes or mixtures like cement pastes is given below. Polytypes are not distinguished; C_2AH_3 , $C_4A(Cl_2)H_{10}$, and C_2ASH_8 (gehlenite hydrate) are omitted.

Composition	Basal Spacing (0001)		Second Order of Basal Spacing		Low Order (hK·O)	
	d, Å		d, Å		d, Å	
	I	I	I	I	I	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
$C_4\bar{A}\bar{C}H_{11}$	7.60	vvs	3.80	ms	2.36	m
$C_4\bar{A}\bar{C}_{0.5}H_{12}$	8.20	vvs	4.11	mw	2.88	vs
$C_4\bar{A}\bar{C}_{0.5}H_{9-10}$	7.77	vvs	3.88	s	2.88	vs
$C_4\bar{A}\bar{S}H_{14-16}$	9.6		4.80		2.87?	vs
$C_4\bar{A}\bar{S}H_{12}$	8.96	vvs	4.46	s	2.87	vs
$C_4\bar{A}\bar{S}H_{10}$	8.20	vvs	4.10	s	2.87	vs
$C_4\bar{A}\bar{S}H_3$	~8.0 (3.05-7.95)	~4.0				

Most of these have a moderate to very strong spacing at 1.66 Å.

As noted earlier, the long spacings fall in the range where errors in d due to errors in measuring two-theta are maximized.

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 Å are usually recognizable; if they are consistently read as 9.73 ± 0.02 and 5.61 ± 0.02 the spacings in between those two may be believed to be 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 $C_4\bar{A}SH_{10}$ it will go to 8.96 but if it is $C_4\bar{A}C_{0.5}H_{12}$ it will not). Without the ability to control and change humidity around the sample it will be extremely difficult to establish the presence of $C_4\bar{A}H_{13}$ as distinguished from $C_4\bar{A}C_{0.5}H_9-10$ (or $C_4\bar{A}SH_8$ --which is not likely to form except in pastes dried at elevated temperature or over $P_{205}^{(25)}$) or to interpret a line at 9.2 Å.

Conclusion

X-ray diffractions permit 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 (26)). 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_4AH_{13} if present in pastes requires control of humidity around the sample because it may easily be confused with other possible constituents.

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

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Table 1

Samples

Cement Pastes		Sample Numbers of Pastes				
Cement	W/C	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 ₃ A)	0.35	17	18	21	23	29
No. 3 (Zero C ₃ 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 β -C ₂ S Hydrated 5.3 years	PCA
37	Tetracalcium aluminate hemicarboxate-12-hydrate	PCA
38	Tetracalcium aluminate carbonate-11-hydrate	PCA
39	Tetracalcium aluminate monosulfate-12-hydrate	NBS
40	Tetracalcium aluminate-10.5-hydrate	PCA
41	Ettringite	NBS
-	Ettringite	PCA

Table 2

Hydrated Phases Examined by Six Laboratories

Sample No.		Laboratory Number					
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
35	Hydrated alite*	x	x	x	-	x	x
36	Hydrated 3-C ₂ 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 monosulfoaluminate**	x	x	x	x	-	x
40	C ₄ AH _{10.5} *	x	x	x	-	x	x
41	Ettringite**	x	x	x	-	x	x
-	Monosulfate (0.75 SO ₃ /Al ₂ O ₃)*	-	-	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*
Diffractionmeter							
General Electric	-	x	x	-	-	-	-
Norelco	x	-	-	x	-	-	x
Rigaki Denki	-	-	-	-	x	-	-
Guinier Camera	-	-	-	-	-	x	-
Monochromator	-	-	-	-	-	x	x**
Radiation	Cu	Cu	Cu	Cu	Cu	CuK α	CuK α
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.

Table 4a

Operating Conditions for Examination of Cement Pastes

	Laboratory 1	Laboratory 2	Laboratory 3
KV of X-ray tube	35	50	50(a) 16(a)
ma of X-ray tube	15	16	21(a)
Apparent watts (b)	525	800	800(a) 1050(a)
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. - 0.03	Beam 1 deg Medium Resolution Soller Medium Resolution Detector: 0.2 deg	7-20 2θ 1 deg 3 deg 0.2 deg 20-60 2θ 3 deg 0.2 deg
Chart full scale deflection	Linear, 240 c/s	Linear, 200 c/s	Logarithmic, 4000 c/s (c)
Time constant	4 sec	3 sec	30 sec/7.5 sec/2 sec (d)
Scale factor	8	-	Not applicable
Multiplier	0.6	-	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 x ma) = apparent watts.

(c) All pastes of 0.18 g were examined in the range 7-20 2θ using a linear scale of 1000 c/s, with time constant = 3 sec, except that the Ca(OH)₂ peak at 18 2-θ was also scanned with tc = 4 sec (samples 1, 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(a)	40(b)	40(c)		40	40
mA of X-ray tube	35	30	35	35	18	35
Apparent watts	1155	1200	1400	525	720	1400
Detector	Scintillation counter		Scintillation counter		Monochromator with Geiger 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
Slits: Divergence	1 deg	1 deg	1 deg	1 deg	1 deg (g)	1 deg
Scatter	1 deg	1 deg	1 deg	1 deg	1 deg	1 deg
Receiving	0.006 in.	0.006 in.	0.006 in.	0.2 mm	0.006 in. ~ 0.06 deg	0.006 in.
	0.006 deg					
Chart full scale deflection	50° c/s	500 c/s	1000 c/s	400 c/s (d)	800 c/s (e)	1600 c/s (f)
Time constant	4	2	2	4	4	8 sec
Pulse height selection	yes	yes	yes	no	no	no

- (a) 33 Kv x 35 ma samples 1 through 16
 (b) 40 Kv x 30 ma samples 17 through 24
 (c) 40 Kv x 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 20, 1 deg divergence and scatter slits; from 20 to 5 20, 0.5 divergence and scatter slits
 (h) Pastes from 60 to 20 20
 (i) Cements 60 to 20 20

Table 5

Strong Lines and Interferences in Portland Cement Pastesd, m x 10⁻¹⁰

9.73 ⁽¹⁾	Ettringite I = 100; 9.6 A $C_4A\bar{S}H_{14-15}$ ⁽²⁾
9.0	$C_4A\bar{S}H_{12}$ (0001) ⁽³⁾
8.2	$C_4A\bar{S}H_{10}$, $C_4A\bar{C}_{0.5}H_{12}$ ⁽⁴⁾ (0001) of both
7.95	C_4AH_{13} ⁽⁶⁾ (0001)
7.77	$C_4A\bar{C}_{0.5}H_9$ ⁽⁴⁾ (0001)
7.62	$C_4A\bar{C}H_{10-11}$ ⁽⁴⁾ (0001)
7.2-7.4	Aluminoferite solid solutions ⁽⁷⁾ ; 7.2 of $C_4A\bar{C}H_6$ ⁽⁴⁾
5.94	Alite ⁽⁷⁾
5.61	Ettringite, I = 31
5.06	Hydrogarnet ⁽⁸⁾ , I = 95
4.90	CH ⁽¹⁾ ; $C_4A\bar{S}H_{12}$ 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	$C_4A\bar{S}H_{12}$; aluminoferite solid solution 3.63-3.70
3.62	C_4AH_{13} weak
3.48	Ettringite, probably not detected.

Table 5 (Continued)

<u>d, m x 10⁻¹⁰</u>	
3.30	Hydrogarnet, weak but not interfered with in paste
3.112	CH, ordinarily masks 3.10 of Hydrogarnet
3.06	C-S-H ⁽⁹⁾
3.04	Alite, Belite, 3.035 of calcite ⁽¹⁾
2.97	Alite
2.88	C ₄ A $\bar{S}$ H ₁₂ , C ₄ A $\bar{S}$ H ₁₀ , C ₄ A $\bar{C}$ _{0.5} H ₁₂ , C ₄ AH ₁₃ ; Belite ⁽⁷⁾ , C ₄ A $\bar{C}$ H ₁₁ 2.86; C ₄ AH ₁₃ 2.86
2.80	C-S-H
2.77	Alite and Belite, Hydrogarnet, Ettringite
2.75-2.74	Alite and Belite; C ₄ A $\bar{S}$ H ₁₂ 2.72
2.70	C ₃ A; 2.69 of C ₄ AH ₁₃
2.63-2.68	Aluminoferite solid solutions
2.628	CH I = 100
2.564	Ettringite
2.54	Belite, C ₄ A $\bar{C}$ _{0.5} H ₁₂ , 2.53 of Hydrogarnet; 2.524 C ₄ A $\bar{C}$ H ₁₁ ⁽⁷⁾
2.495	Calcite, C ₄ AH ₁₃ , C ₄ A $\bar{C}$ H ₁₁
2.47	C ₄ AH ₁₃
2.45	C ₄ AH ₁₃ , C ₄ A $\bar{S}$ H ₁₂ , C ₄ A $\bar{C}$ _{0.5} H ₁₂
2.42	C ₄ A $\bar{S}$ H ₁₂ , C ₄ A $\bar{C}$ H ₁₁
2.40	CaO - improbable in paste
2.35	C ₄ A $\bar{C}$ _{0.5} H ₁₂ , 2.34 of C ₄ A $\bar{C}$ H ₁₁
2.285	Calcite - weak
2.27	Hydrogarnet, I = 100; 2.26 of C ₄ A $\bar{S}$ H ₁₂
2.23	Ettringite, C ₄ A $\bar{C}$ _{0.5} H ₁₂

Table 5 (Continued)

<u>d, m x 10⁻¹⁰</u>	
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 ₄ A ⁻ SH ₁₂
2.00	Hydrogarnet I = 95
1.927	CH
1.796	CH
1.687	CH
1.66	C ₄ A ⁻ SH ₁₂ , C ₄ A ⁻ C _{0.5} H ₁₂ , C ₄ A ⁻ CH ₁₁ , C ₄ AH ₁₃

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- (^c) Data from this program.

Table 6

Cement No. 1: Constituents of Pastes with W/C = 0.35

	Curing, Days				
	<u>1</u>	<u>7</u>	<u>28</u>	<u>90</u>	<u>365</u>
Ettringite	x	x	x	x	x
C ₄ ASH ₁₂	-	x	x	x	x
Calcium hydroxide	x	x	x	x	x
Hydrogarnet	-	tr?	tr?	x	x
C ₄ A $\bar{C}$ H ₁₁	-	-	-	x	tr
C ₄ AH _x	-	x	x	x	-
C ₃ AH ₆	-	-	-	?	-
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
C ₃ 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

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

	<u>Curing, Days</u>				
	<u>1</u>	<u>7</u>	<u>28</u>	<u>90</u>	<u>365</u>
Ettringite	x	x	x	x	tr?
C ₄ ASH ₁₂	tr?	x	x	x	x
Calcium hydroxide	x	x	x	x	x
Hydrogarnet	-	-	-	-	tr?
C ₄ ACH ₁₁	-	-	x	x	
C ₄ AH _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 A	x	x	x	-	-

NOTE: tr? = possible trace.

Laboratories Reporting Each Constituent

Ettringite	5	5	5	4	1
C ₄ ASH ₁₂	2	4	5	5	2
Calcium hydroxide	7	7	7	7	6
Hydrogarnet	-	-	-	-	1
C ₄ ACH ₁₁	-	-	2	1	-
C ₄ AH _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 A	5	2	2	-	-

Table 8

Cement No. 3: Constituents of Pastes with W/C = 0.35

	Curing, Days				
	<u>1</u>	<u>7</u>	<u>28</u>	<u>90</u>	<u>365</u>
Ettringite	x	x	x	x	tr
C ₄ A $\bar{S}$ H ₁₂	tr?	tr	tr	tr	tr?
Calcium hydroxide	x	x	x	x	x
C ₄ AH _x	tr	-	-	-	-
C-S-H	x	x	x	x	x
Alite	x	x	x	x	x
Belite	x	x	x	x	x
Aluminoferite	x	x	x	x	x

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

Laboratories Reporting Each Constituent

Ettringite	4	3	4	5	2
C ₄ A $\bar{S}$ H ₁₂	1	2	2	2	1
Calcium hydroxide	7	7	7	7	6
C ₄ AH _x	1	-	-	-	-
C-S-H	1	4	4	5	3
Alite	5	5	5	5	5
Belite	5	4	4	3	2
Aluminoferite	6	6	6	6	6

Table 9

Cement No. 1: Constituents of Pastes of W/C = 0.65

	<u>Curing, Days</u>				
	<u>1</u>	<u>7</u>	<u>28</u>	<u>90</u>	<u>365</u>
Ettringite	x	x	x	x	-
C ₄ A ₃ H ₁₂	x	x	x	x	x
Ca(OH) ₂	x	x	x	x	x
Hydrogarnet	tr?	tr	tr	tr	tr
C ₄ AH _x	-	-	P	D	-
C ₄ A ₃ H ₁₁	-	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 ₃ A	x	x	tr?	-	-
Aluminoferriite 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 ₄ A ₃ H ₁₂	1	6	5	6	5
Ca(OH) ₂	7	7	7	7	6
Hydrogarnet	1	2	2	2	2
C ₄ AH _x	-	-	1	1	-
C ₄ A ₃ H ₁₁	-	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 ₃ A	5	3	1	-	-
Aluminoferriite 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

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

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

Laboratories Reporting Each Constituent

Ettringite	6	5	5	4	4
C ₄ A ₃ H ₁₂	-	7	7	6	5
Ca(OH) ₂	7	7	7	7	6
C ₄ AH _x	-	-	-	-	1
C ₄ A ₃ H ₁₁ (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 ₃ A	5	2	2	1	-
Calcite	1	-	-	-	-

Table 11

Cement No. 3: Constituents of Pastes of W/C = 0.65

	Curing, Days				
	<u>1</u>	<u>7</u>	<u>28</u>	<u>90</u>	<u>365</u>
Ettringite	x	x	x	x	x
C ₄ A $\bar{S}$ H ₁₂	-	tr	tr?	tr	?
Ca(OH) ₂	x	x	x	x	x
C ₄ AH _x	-	tr	-	tr	-
C ₄ A $\bar{C}$ H ₁₁	-	-	-	-	tr?
C-S-H	x	x	x	x	x
Alite	x	x	x	x	tr
Belite	x	x	x	x	x
Aluminoferriite 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 ₄ A $\bar{S}$ H ₁₂	(Total of 3)	2	1	2	1
Ca(OH) ₂	7	7	7	7	6
Hydrogarnet	1	1	-	-	-
C ₄ AH _x	-	1	-	1	-
C ₄ A $\bar{C}$ H ₁₁	-	-	-	-	1
C-S-H	1	4	4	4	3
Alite	5	5	4	4	1
Belite	5	4	3	2	1
Aluminoferriite solid solution	6	6	6	6	5
Calcite	1	1	1	1	-

Table 12

Intensity Relations Among Some Constituents
of Pastes of 0.65 Water-Cement Ratio⁽¹⁾

	Peak Height Above Background, Counts/Second				
	Age, Days				
	1	7	28	90	365
<u>Cement No. 1 - Type 1</u>					
Ettringite	87	21	<5 (est)	tr (est)	-
C ₄ ASH ₁₂	-	41	72	74	58
C ₄ A $\bar{C}$ H ₁₁ (Note 2)	-	pr	pr	pr	pr
CH	489	417	702	842	679
<u>Cement No. 2 - White</u>					
Ettringite	47	28	18	5 (est)	tr
C ₄ ASH ₁₂	-	26	39	41	34
C ₄ A $\bar{C}$ H ₁₁	-	tr?	tr	pr	pr
CH	653	848	692	492	435
<u>Cement No. 3 - Zero C₃A</u>					
Ettringite	20	20	20	5 (est)	<5 (est)
C ₄ ASH ₁₂	-	tr	tr?	tr	?
CH	460	586	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 Ni 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 (C₄ASH₁₂), and 4.92 Å (CH).

(2) C₄A $\bar{C}$ H₁₁ 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		
<u>d, Å</u>	<u>I*</u>		<u>d, Å</u>	<u>I</u>	
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	vww	C-S-H
2.786	5	C-S-H	2.83	vww	?
2.629	100	CH	2.63	vvs	CH
			2.46	vww	CH
1.926	43	CH	1.93	vs	CH
1.816	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			

* Net 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.

Table 14

Sample 36: Hydrated α -C₂S Cured 5.3 Years

Laboratory 3			Laboratory 6		
d, Å	I*		d, Å	I	
4.91	100	CH	4.91	ms	CH
4.6	1	β -C ₂ S	3.34	vw	C ₂ S
3.23	2	β -C ₂ S	3.11	ms	CH
3.11	16	CH	3.06	ms/b	C-S-H
3.052	31	C-S-H, CaCO ₃ ?**	2.97	w/b	C-S-H
2.966	21		2.88	mw	C ₂ S
2.877	16	β -C ₂ S	2.79	m	C ₂ S, C-S-H
2.815	17	?	2.75	w	C ₂ S
2.781	21	β -C ₂ S	2.63	vvs	CH
2.739	19	β -C ₂ S	2.61	w	C ₂ S
2.720	10	β -C ₂ S	2.44	w	CH, C ₂ S
2.627	60	CH	2.41	vw	C-S-H, C ₂ S
2.547	2	β -C ₂ S	2.28	w	C ₂ S
2.442	4	β -C ₂ S, CH	2.19	mw	C ₂ S
2.404	4	β -C ₂ S	2.165	rw	C ₂ S
2.27	3	β -C ₂ S	2.08	vvw	C ₂ S
2.18	7	β -C ₂ S	2.05	vvw	C ₂ S
2.16	2	β -C ₂ S	1.98	vw	C ₂ S
2.15	1	β -C ₂ S	1.93	ms	CH
2.08	2	β -C ₂ S	1.825	ms/b	C-S-H
2.026	3	β -C ₂ S	1.799	s	CH
1.984	4	β -C ₂ S, CH	1.69	m	CH
1.920	23	CH	1.628	w	CH
1.894	2	β -C ₂ S			
1.819	12	C-S-H***			
1.790	9	CH			
1.707	1	β -C ₂ S			
1.685	6	CH			
1.627	1	β -C ₂ S			
1.549	2	β -C ₂ S			
1.524	2	β -C ₂ S			
1.482	3	CH			
1.440	3	CH			

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

** Halo from 26 to 38 two-theta.

*** About two theta wide at base.

Table 15

Sample 37: Tetracalcium Aluminate Hemicarboxate-12-Hydrate

Laboratory 5		Laboratory 6		
d,A	I	d,A	I	
8.12	vvs	8.2	10	
		7.8	1	?
5.405	vW			
5.12	w	5.11	3	C ₃ AH ₆
4.895	w			
		4.62	4	
		4.43	2	C ₃ AH ₆
4.104	vs	4.09	7	
3.873	s	3.87	9	
		3.77	1	
		3.50	2	
3.359	w	3.35	2	C ₃ AH ₆
3.245	vW			
3.134	vW	3.13	2	C ₃ AH ₆
		3.02	1	
2.88	m	2.88	9	
		2.83	3	
2.808	w	2.80	3	C ₃ AH ₆
2.728	m	2.72	8	
		2.62	2	
2.545	m	2.54	8	
		2.47	1	C ₃ AH ₆ ?
2.448	m	2.44	9	
2.358	m	2.35	6	
2.319	w	2.31	4	
2.293	ms	2.29	3	C ₃ AH ₆
		2.22	4	
		2.20	2	
2.166	w	2.16	2	
		2.07	1	
2.043	m	2.03	5	C ₃ AH ₆ ?
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	C ₃ AH ₆ ?
		1.70	1	
		1.68	1	
		1.67	1	C ₃ AH ₆
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 5		
d, Å	I*		d, Å	I	
7.62	100		7.6	10	
5.71	<1		5.72	1	
5.14	<1	C ₃ AH ₆	5.12	2	C ₃ AH ₆
4.93	<1		4.94	1	
4.85	1	Gibbsite?	4.88	1	
			4.82	1	
4.68	<1	Bayerite?	4.56	2	
4.49	1	C ₃ AH ₆	4.46	3	C ₃ AH ₆ ?
4.36	2		4.34	4	
3.66	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	C ₃ AH ₆	3.34	1	C ₃ AH ₆
3.30	<1		3.29	1	
3.144	<1	C ₃ AH ₆	3.13	1	C ₃ AH ₆
3.03	<1	Calcite	2.86	9	
2.559	7		2.85	1	
			2.82	3	
			2.51	1	C ₃ AH ₆
2.779	2		2.78	5	
2.725	4		2.71	7	
2.654	1		2.65	1	
			2.62	1	
2.576	<1		2.58	2	
2.526	?		2.53	7	
			2.52	2	
2.45	5		2.49	6	
			2.48	7	
2.404	3		2.44	6	
2.422	12		2.42	2	
2.34	11		2.33	8	
2.24	2	C ₃ AH ₆ ?	2.29	3	C ₃ AH ₆ ?
			2.26	1	
2.239	1		2.23	3	
2.214	<1	Bayerite?	2.21	3	
2.167	5		2.165	1	
			2.16	3	
2.14	<1		2.13	2	
2.118	5		2.11	5	
2.097	5		2.09	3	
2.065	<1		2.06	2	

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

Table 16 (Continued)

Laboratory 3			Laboratory 6		
<u>d,A</u>	<u>I*</u>		<u>d,A</u>	<u>I</u>	
2.036	2	C ₃ AH ₆ in part?	2.03	2	
2.028	2		2.02	1	C ₃ AH ₆
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	
1.862	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	C ₃ AH ₆	1.74	1	
1.728	<1		1.72	1	
1.714	1		1.71	1	
1.690	<1		1.69	1	
1.679	<1	C ₃ AH ₆	1.68	1	
1.665	2		1.67	1	C ₃ AH ₆
			1.66	5	

and five lines to 1.60

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

Table 17

Sample 39: Tetracalcium Aluminate Monosulfate-12-Hydrate

Laboratory 3			Laboratory 6		
d, Å	I*		d, Å	I	
9.8	2	Ettringite	9.8	1	Ettringite
8.96	100		9.0	10	
5.60	<1	E	5.62	1	E
4.90	1		4.92	3	
4.68	<1	E	4.70	1	E
4.47	32		4.48	8	
4.00	12		4.00	9	
3.88	<1	E	3.88	1	E
3.65	1		3.66	3	
3.47	<1	E	3.48	1	E
3.24	<1	E			
3.031	<1	Calcite			
2.879	6		2.88	9	
2.778	1	E in part?	2.78	1	E?
2.741	3		2.74	6	
2.615	<1	E?	2.63	1	E? or Ca(OH) ₂ ?
2.559	<1	E	2.56	1	E
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	E
2.149	<1	E	2.19	3	
2.088	1		2.15	1	E
2.072	6		2.09	2	
2.060	1		2.07	6	
1.993	2		2.00	3	
1.879	<1		1.91	2	
1.867	<1		1.88	2	
1.825	3		1.87	2	
1.816	1		1.83	4	
1.788	<1		1.81	3	
1.765	1		1.78	2	
1.742	<1		1.77	2	
1.691	<1		1.74	1	
1.661	2		1.69	1	
1.634	1		1.66	7	
			1.64	1	
			1.63	5	

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

Table 17 (Continued)

<u>Laboratory 3</u>		<u>Laboratory 6</u>	
<u>d, Å</u>	<u>I</u>	<u>d, Å</u>	<u>I</u>
1.589	2	1.59	2
1.558	<1	1.56	3
1.544	<1	1.54	3
1.522	<1		
1.504	<1		
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.

Table 18

Unstable $C_4AH_{10.5}$

Laboratory 1			Laboratory 3			Laboratory 5		
d, Å	I		d, Å	I		d, Å	I	
7.91	100	C_4AH_{13}	8.20	100	H	8.19	ss	H
7.60	7	M				7.81	s	$C_4AC_{0.5}H_{10}$
			5.25	<1				
5.13	2	C_3AH_6	5.12	16	C_3AH_6	5.13	s	C_3AH_6
4.91	<1	CH	4.89	28	CH	4.91	s	CH
			4.62	<1	H	4.785	ww	H
4.44	<1	C_3AH_6	4.43	7	C_3AH_6	4.440	m	C_3AH_6
3.96	22	C_4AH_{13}	4.09	28	H	4.105	s	H
3.73	2	M	3.86	4	H	3.870	b	H
			3.50	<1	H			
3.36	1	C_3AH_6	3.348	8	C_3AH_6	3.336	m	C_3AH_6
			3.248	<1				
			3.136	6	C_3AH_6	3.140	w	C_3AH_6
			3.11	2	CH	3.115	w	CH
			2.877	2	H	2.880	ww	H
2.81	1	C_3AH_6	2.806	12	C_3AH_6	2.813	ss	C_3AH_6
						2.731	wwb	
			2.712	1	H			
			2.676	1	C_3AH_6	2.682	ww	C_3AH_6
2.64	1	CH	2.624	8	CH, H	2.629	m	CH, H
			2.562	3	C_3AH_6	2.571	w	C_3AH_6
			2.540	2	H			
2.47	1	C_3AH_6	2.460	5	C_3AH_6	2.469	w	C_3AH_6
			2.443	3	H, CH			
			2.350	1	H			
2.31	2	C_3AH_6	2.290	16	C_3AH_6	2.298	m	C_3AH_6
			2.210	2	C_3AH_6 , H	2.209	b	C_3AH_6
			2.161	<1	H			
			2.116	<1				
2.00	2	C_3AH_6	2.036	15	C_3AH_6 , H	2.040	s	C_3AH_6 , H
1.9	1	C_3AH_6	1.984	2	C_3AH_6 , H	1.987	ww	C_3AH_6 , H
			1.922	5	CH	1.926	w	CH
			1.650	<1	H			

NOT: H = $C_4AC_{0.5}H_{10}$; M = $C_4AC_{0.5}H_{12}$. References: H. F. W. Taylor, The Chemistry of Cements, Vol 2, pp 394-396; cards 3-125, 4-733, Joint Committee on Powder Diffraction Standards; M. H. Roberts, Calcium Aluminate Hydrate, and Related Basic Salt Solid Solutions, 5th Int Symposium on the Chemistry of Cements, Tokyo, 1968, Vol 2, 100.

Table 18 (Continued)

<u>Laboratory 1</u>			<u>Laboratory 3</u>			<u>Laboratory 5</u>		
<u>d,A</u>	<u>I</u>		<u>d,A</u>	<u>I</u>		<u>d,A</u>	<u>I</u>	
			1.851	<1	H			
			1.810	3	C ₃ AH ₆ , H	1.814	w	C ₃ AH ₆
			1.792	1	H, CH	1.796	wwb	
			1.774	<1	H	1.776	wwb	H
1.74	<1	C ₃ AH ₆ , H	1.740	6	C ₃ AH ₆ , H	1.745	w	C ₃ AH ₆ , H
			1.707	4	C ₃ AH ₆	1.711	w	
1.68	<1	C ₃ AH ₆	1.676	9	C ₃ AH ₆ , CH	1.680	m	C ₃ AH ₆
			1.662	1	H			
			1.630	<1	H			
			1.594	2	C ₃ AH ₆	1.597	ww	C ₃ AH ₆
			1.574	1	C ₃ AH ₆	1.572	ww	C ₃ AH ₆
			1.540	<1	H			
			1.522	<1	H	1.482		
			1.500	<1	H			
			1.480	1	C ₃ AH ₆ , CH	1.482	ww	C ₃ AH ₆ , CH

Table 19

Sample 41: Ettringite

Laboratory 3			Laboratory 6	
d, Å	I*		d, Å	I
10.72	2	Cu K ₃ of 9.75	11.0	2
9.75	100		9.8	10
8.34	9	Not ettringite	8.9	4
7.19	1		7.2	2
5.79**	4		5.81	3
5.62	50		5.63	8
4.97	12		4.99	5
4.36	4		4.86	2
4.70	18		4.72	8
4.43	<1			
4.02	4		4.03	3
3.67	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
2.306	3		2.81	2
2.774	21		2.78	9
2.717	1		2.72	1
			2.69	2
2.608	6		2.68	3
2.612	11		2.62	5
2.562	13		2.57	9
2.522	2		2.52	2
2.435	2		2.49	3
2.409	3		2.41	4
2.343	2		2.35	4
			2.32	1
			2.28	1
2.229	4		2.23	4
2.208	21		2.21	9
2.164	4		2.18	3
2.151	11		2.15	7
			2.13	1
2.123	3		2.12	2
2.079	<1		2.08	2
2.0	2		2.06	3

* Intensity expressed as net peak height referred to net peak height of 9.75 Å line.

** Not on card J-414 of Joint Committee Powder Diffraction File

Table 19 (Continued)

Laboratory 3		Laboratory 6	
<u>d, Å</u>	<u>I*</u>	<u>d, Å</u>	<u>I</u>
2.030	<1	2.01	2
2.003	<1	1.98	2
1.976	1	1.95	4
1.973	1	1.93	1
1.943	6	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.

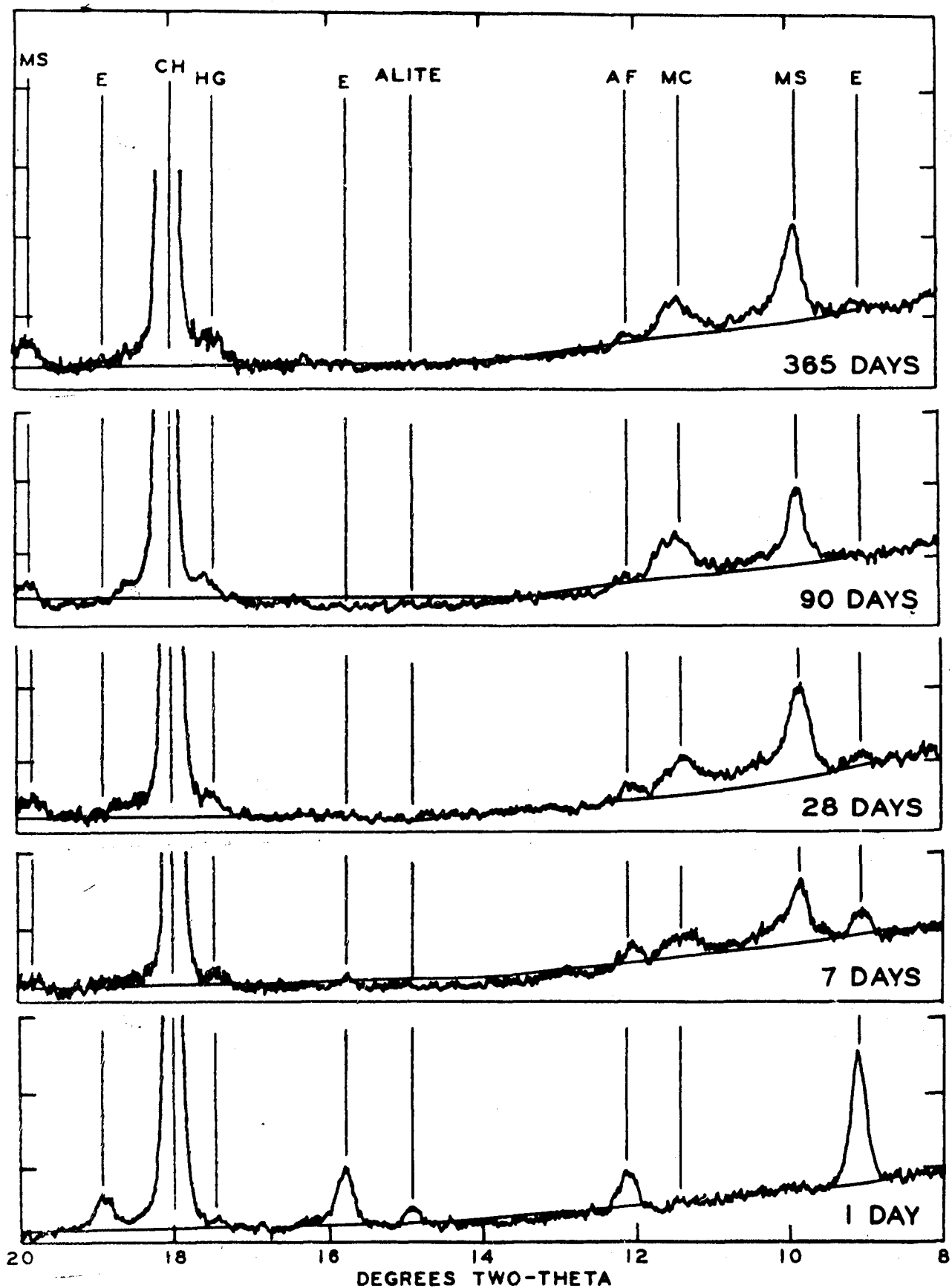


Figure 1. Partial diffractometer charts of pastes of 0.65 w/c, cement No. 1. Beam slit 1° , 3° beam slit as Soller, 0.2° detector slit, scanning speed 0.2° per minute, linear rate meter operation with full-scale deflection 1000 counts per second, time constant 8 sec; MS = C_4ASH_{12} . MC = C_4ACH_{11} . HG = hydrogarnet

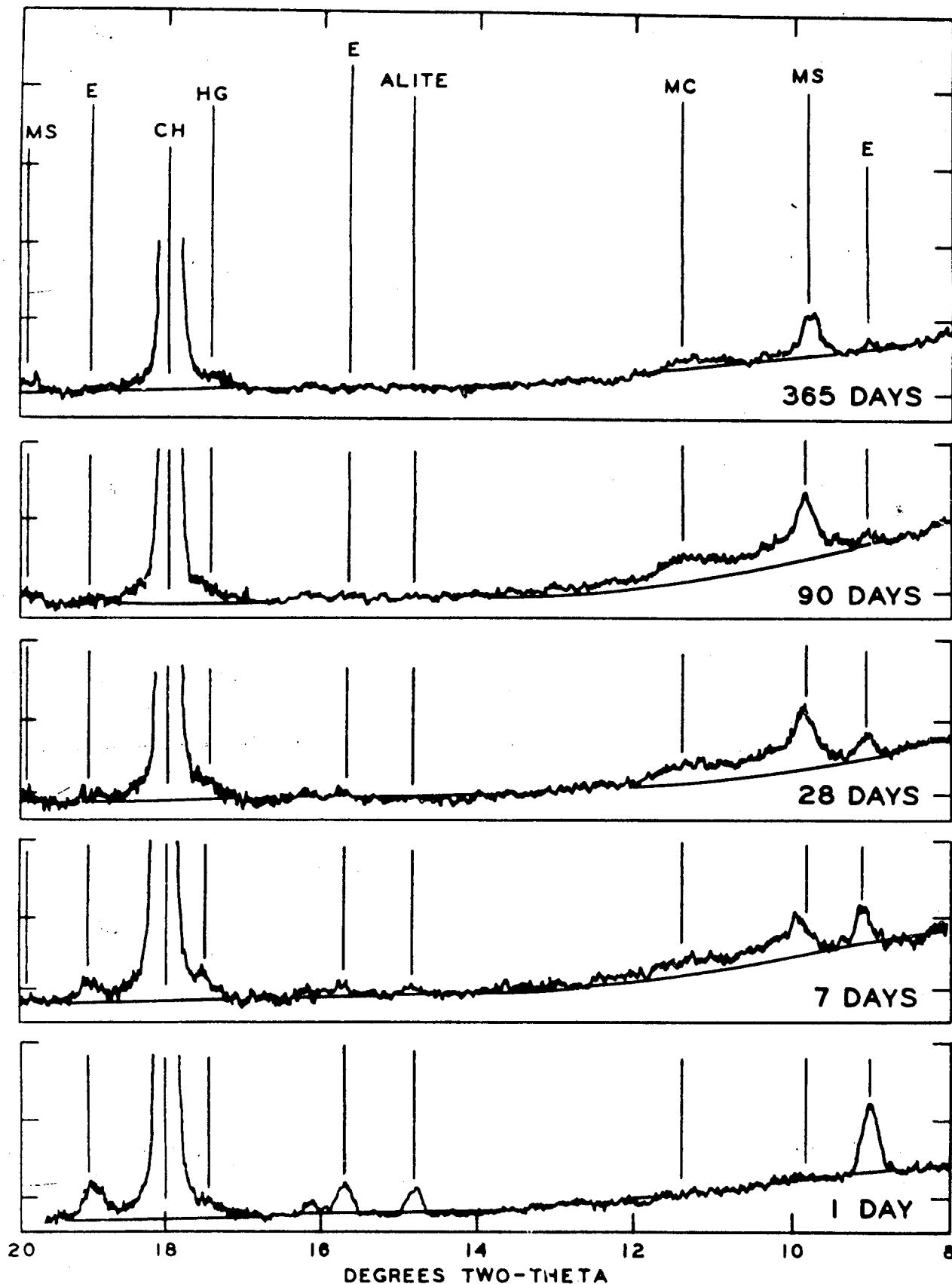


Figure 2. Partial diffractometer charts of pastes of 0.65 w/c, cement No. 2, as in fig. 1. The hydrogarnet line at 17.5 two-theta is shown but evidence of its presence is suggested only at 7 days. The broad indefinite bulge marked MC(=C₄ACH₁₁) in charts of 7 through 90 day pastes covers a range of spacings and alternate identifications could be made.

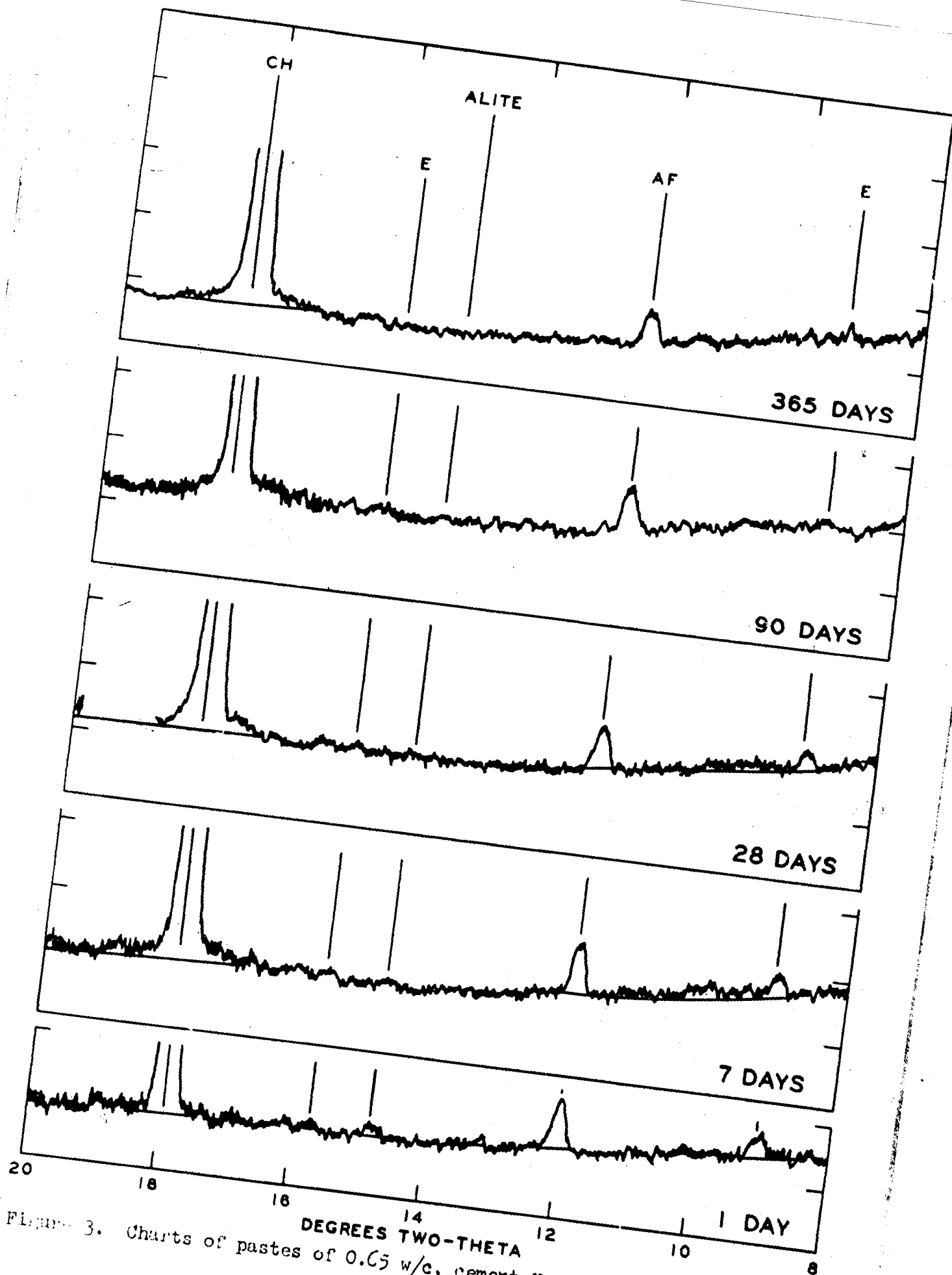


Figure 3. Charts of pastes of 0.65 w/c, cement No. 3, as in figs. 1 and 2.

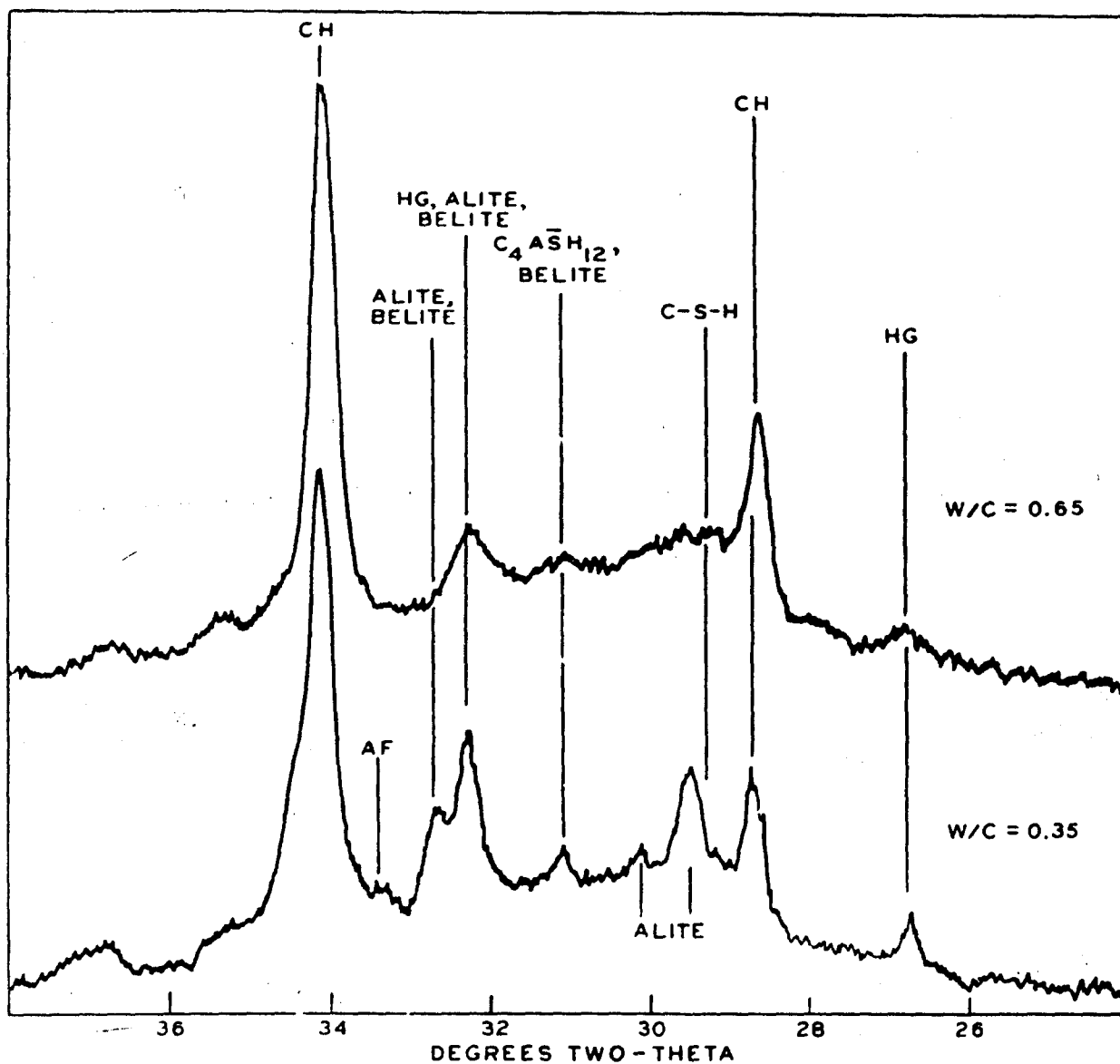


Figure 4. Partial diffractometer charts of 365-day pastes, cement No. 1. Conditions as in figs. 1 through 3 except logarithmic rate meter operation with time constants 30, 7.5, and 2 sec in the first, second, and third decades of the scale. Residual silicates present in 0.35 w/c paste.

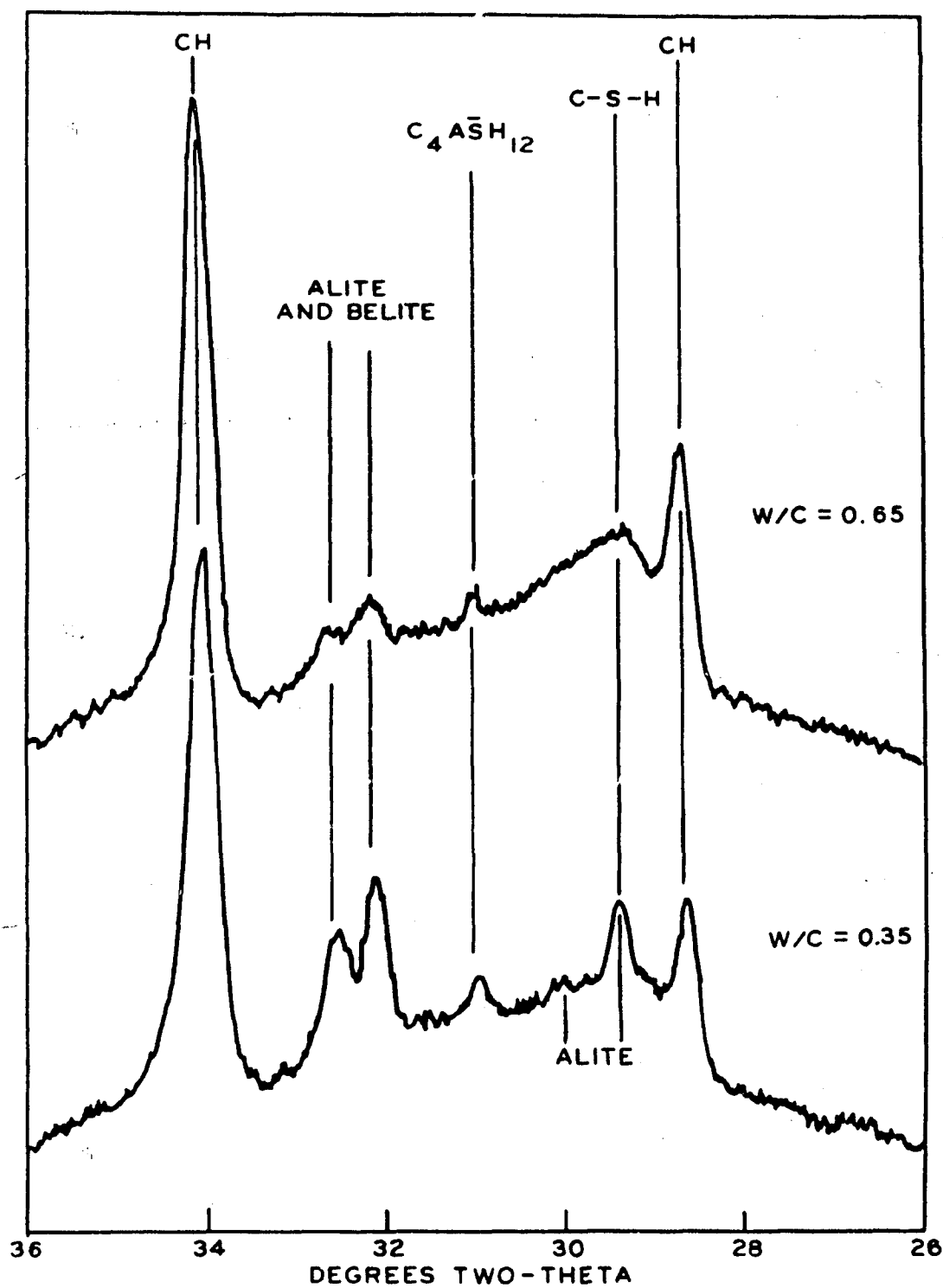


Figure 5. Charts of 365-day pastes of cement No. 2. Both pastes contain some residual silicates.

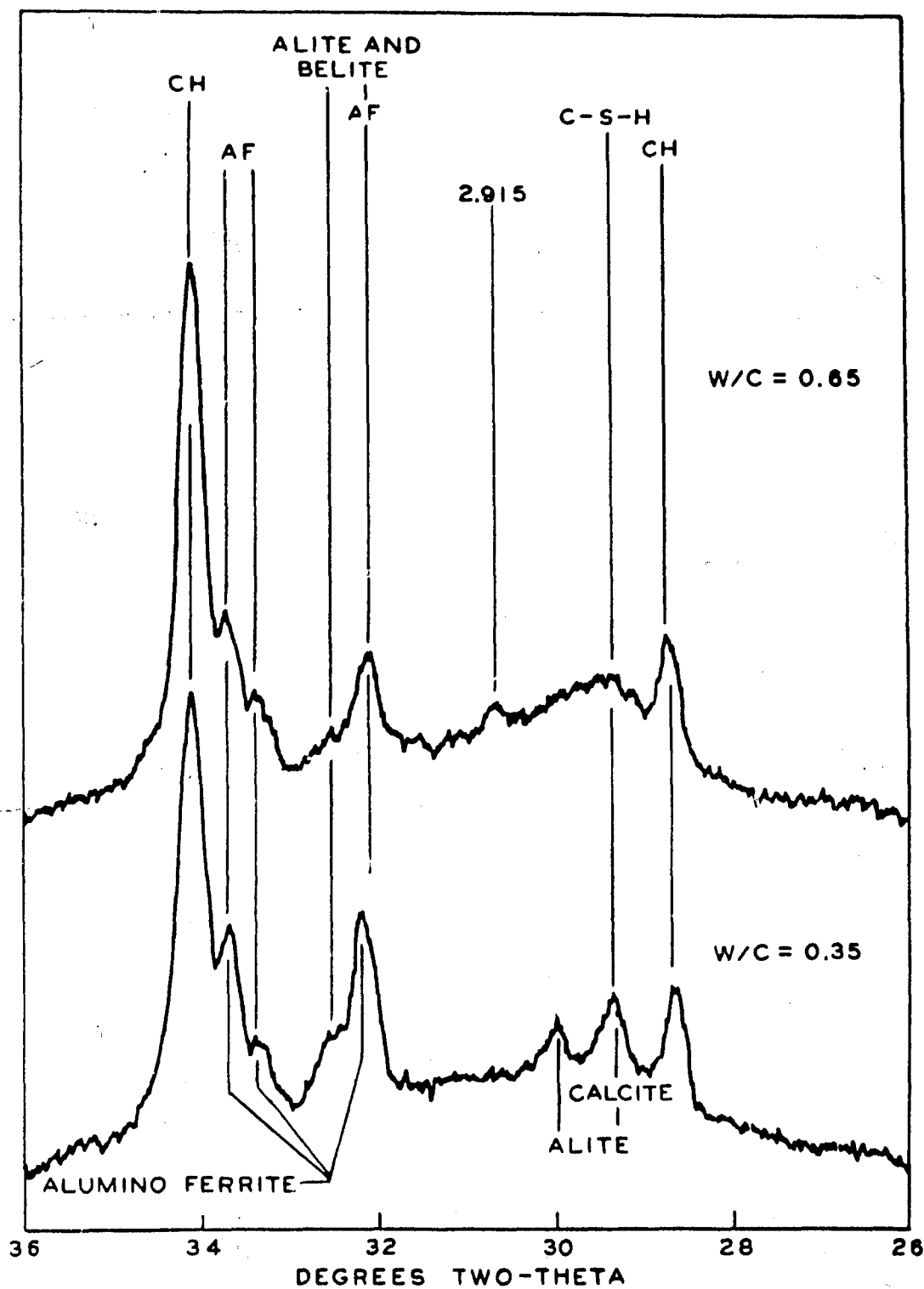


Figure 6. Charts of 365-day pastes of cement No. 3. Strong residual aluminoferrite solid solutions and some silicates. Spacing at 2.915 unidentified.

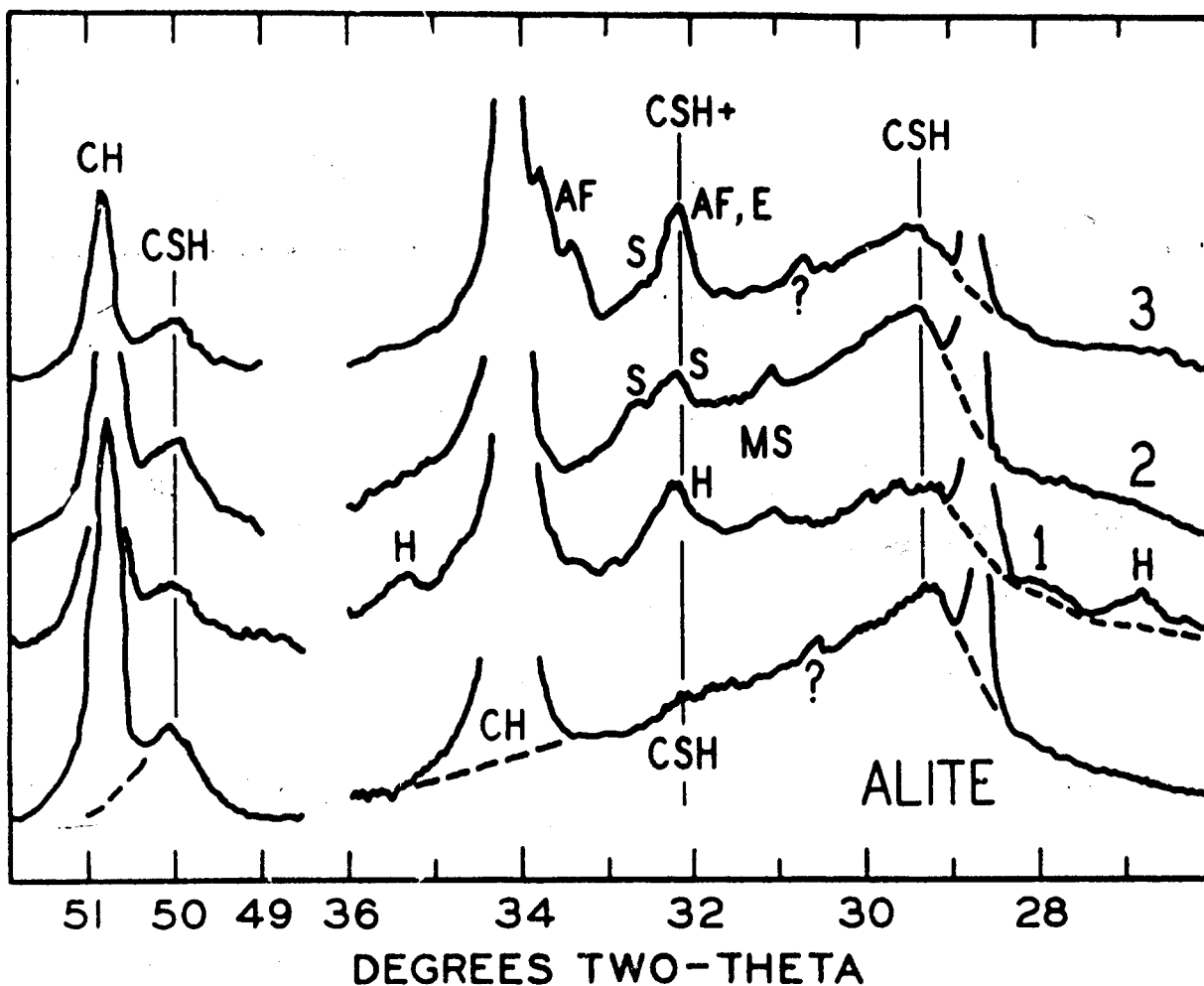


Figure 7. Charts of 0.65 w/c 365-day pastes of all three cements, with 1.5-year-hydrated alite as comparison. The alite spacing between 29° and 30° appears longer than those of the cements. C-S-H = C-S-H gel; S = silicates (alite and belite).