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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  $\text{Al}_2\text{O}_3$ , 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  $\text{CO}_2$ , 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).

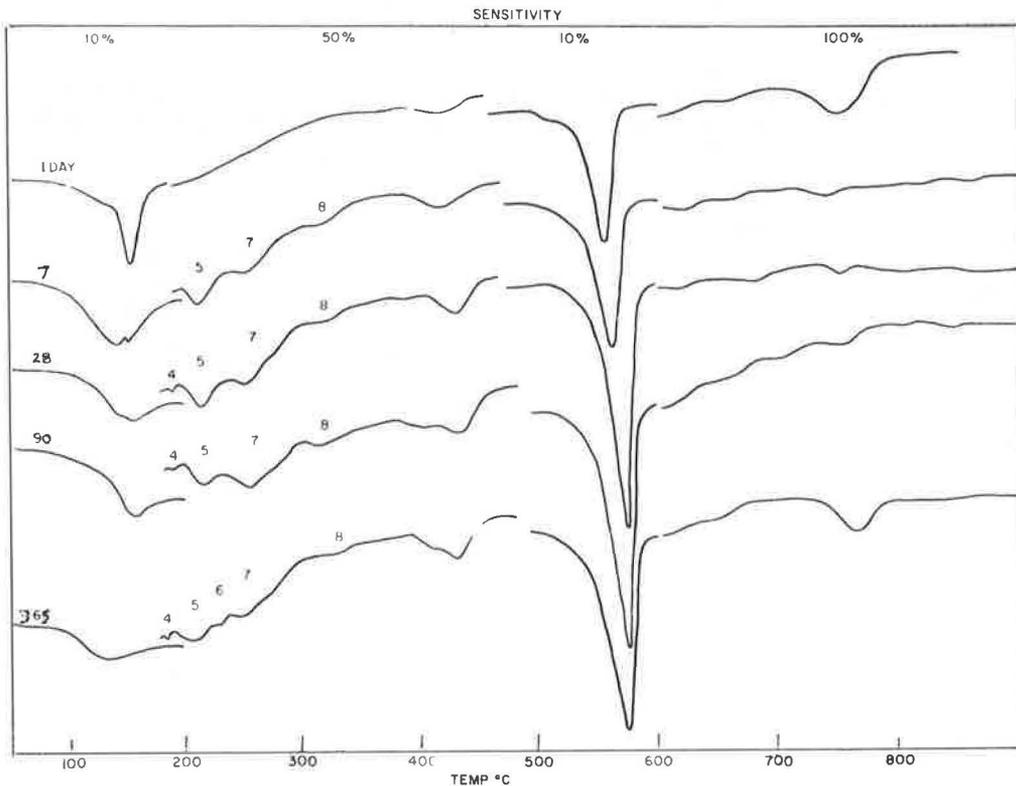


Figure 2. No. 1, monosulfate (Sample No. 39 in Program); No. 2, monosulfate from BRS; No. 3, monosulfate, old sample from NBS; No. 4, solid solution with  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio of 0.75; No. 5, monocarboaluminate (No. 38 in Program); and No. 6, hemicarboaluminate (No. 37 in the Program)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

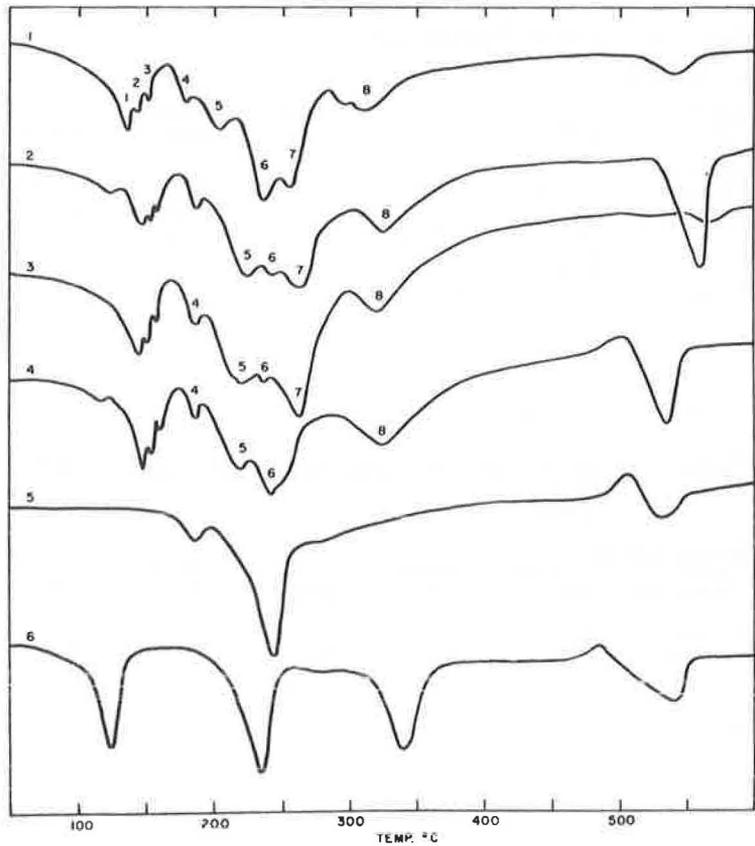
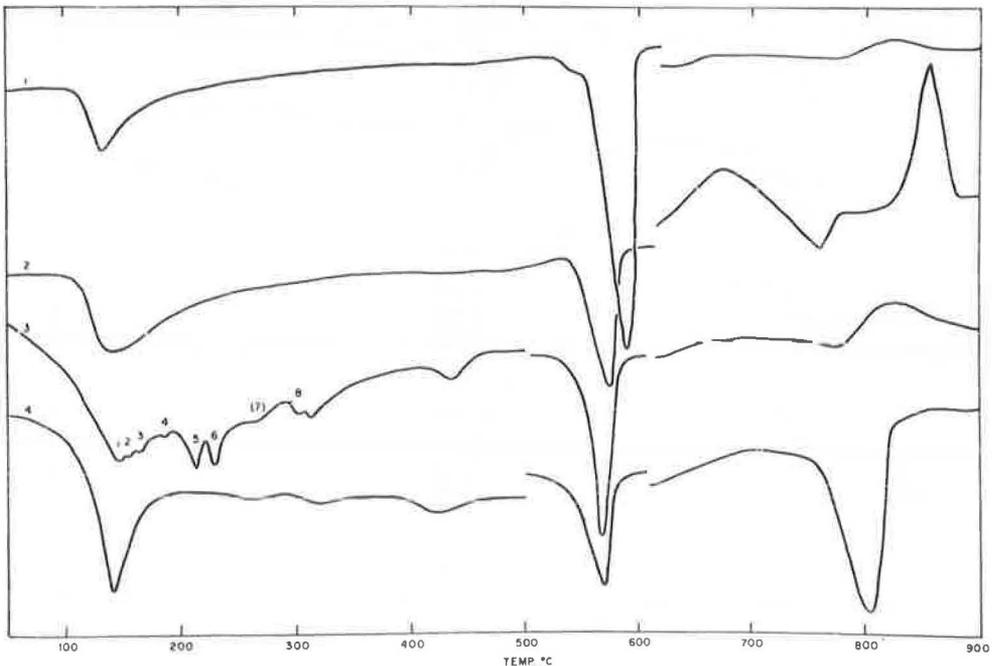


Figure 3. No. 1 is hydrated alite (Sample No. 35 in Program); No. 2 is hydrated  $\beta\text{-C}_2\text{S}$  (Sample No. 36 in Program); Nos. 3 and 4 are Long-Time Study Cements 18 and 43, respectively; hydrated for 20 years (Lab. No. 2).



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.

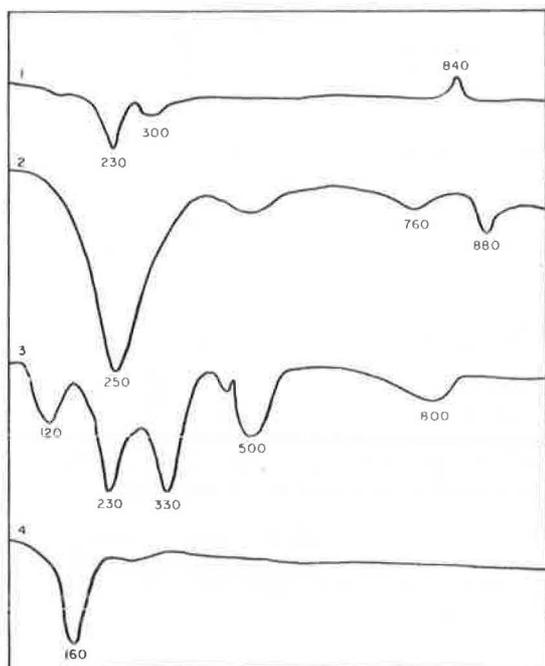


Figure 5. Samples used in Program tested by Lab. No. 7; No. 1 is monosulfate; No. 2 is monocarboaluminate; and No. 3 is ettringite.

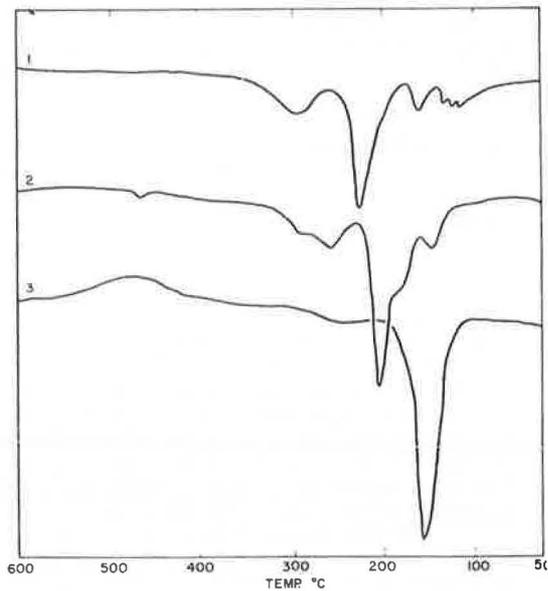


Figure 6. Cement 1 with 0.65 and 0.35 w/c cured to 1 to 365 days (Lab. No. 1).

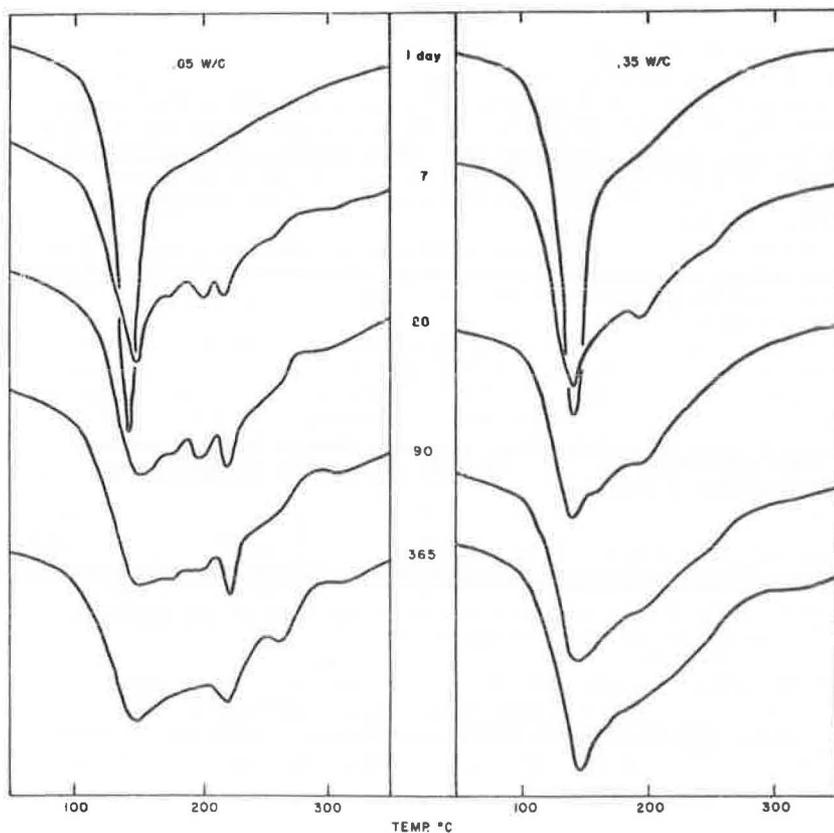


Figure 7. Cement 1 with 0.65 w/c cured 1 to 365 days (Lab. No. 4).

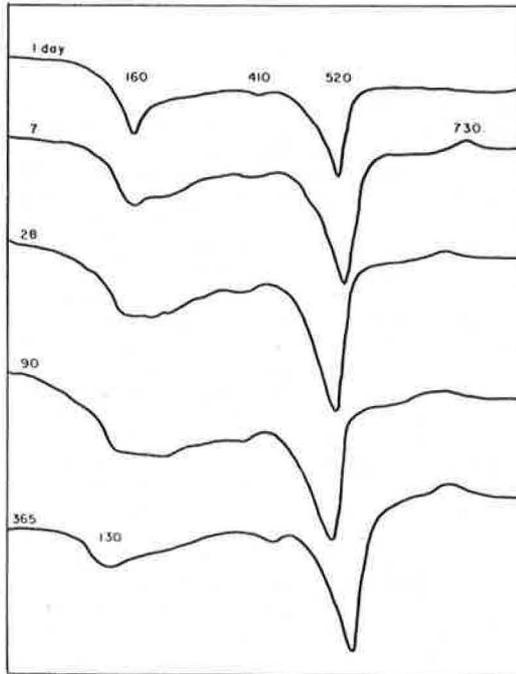


Figure 8. Cement 1 with 0.65 and 0.35 w/c cured 1 to 365 days (Lab. No. 6).



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 → monosulfate → 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).

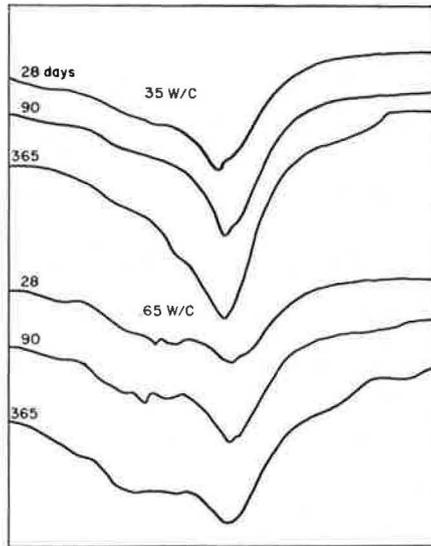
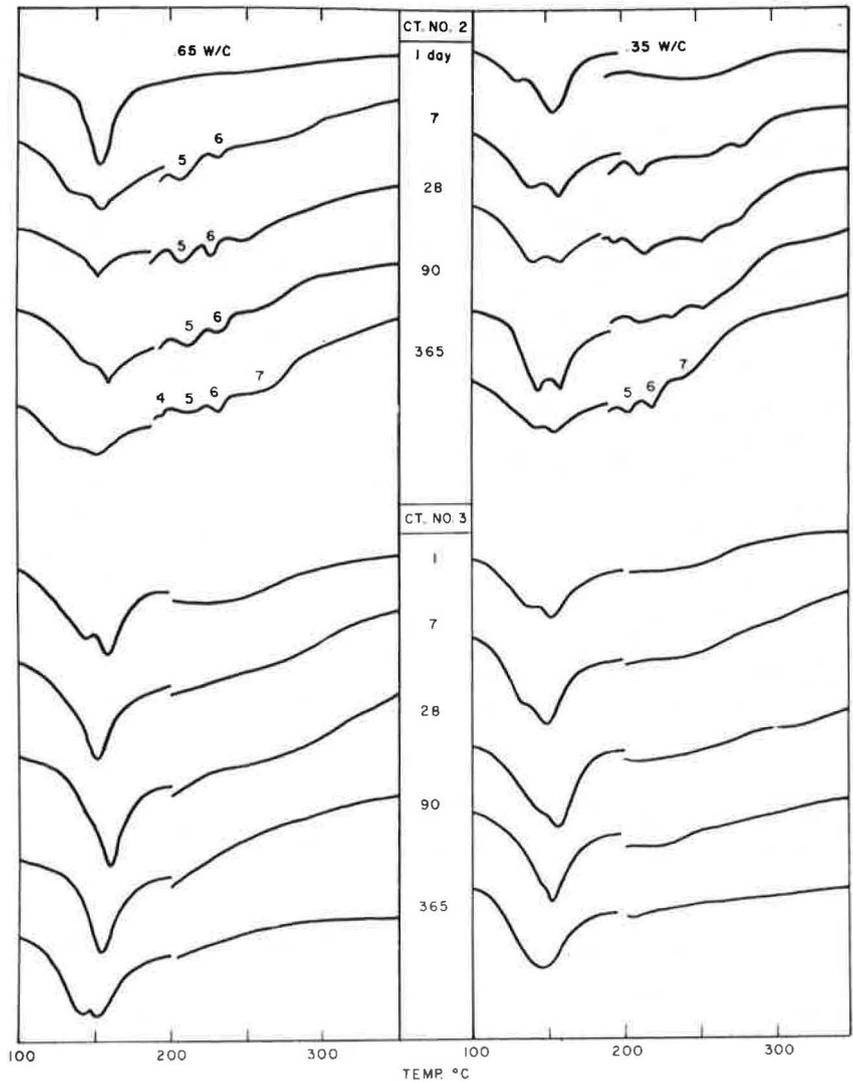


Figure 10. Cements 2 and 3 with 0.65 and 0.35 w/c cured 1 to 365 days (Lab. No. 2).



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  $cm^{-1}$ .