THE SIGNIFICANCE OF EARLY HEAT LIBERATION OF CEMENT PASTE

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SYNOPSIS

This paper concerns differences in rates of heat generation of cements during the first 24 hours after mixing, and the probable significance of the differences A "conduction" calorimeter is described that measures instantaneous rates of heat liberation The results from this calorimeter form the basis of the paper

Plotted curves of the rates of heat liberation of cements for the first 24 hours after mixing show wide differences, suggesting that the early heat characteristics may be a sensitive index to the performance of a cement The following properties of cement are shown to be related to early heat of hydration setting times, early strength, temperature rise of concrete in thin slabs, and probably bleeding of concrete

The early heat characteristics of cements are affected by the following factors fineness, composition, gypsum content, cooling treatment of cement clinker, temperature of hydration, "conditioning" on ageing of cement, and the presence of extraneous materials An example of the effect of these variables is the fact that a few per cent of an active puzzolanic material may increase the maximum rate of heat liberation by a hundred per cent or more, although it may reduce the total heat liberation

The preliminary studies of early-heat characteristics presented in this paper indicate that the conduction calorimeter is a good tool for research The early heat of hydration may provide a guide to improving the quality and uniformity of cements when the significance of results is more fully understood

The purpose of this paper is to present the preliminary results of studies on the early heat of hydration of cement The different heat characteristics of individual cements will be shown and the correlation of these characteristics with the performance of the cement will be attempted While it is believed that early-heat measurements have possibilities of worth while applications, the present paper is devoted only to indicating the apparent significance of the early-heat measurements The studies thus far are instructive but are not exhaustive enough to recommend early-heat measurement for purposes other than research

TEST METHODS AND APPARATUS

Because of the peculiar variations in early heat liberation of cement, three kinds of calorimeters were employed to obtain the complete heat-liberation record for 24 hours after mixing One simple calorimeter was used to determine the heat liberated up to one half hour, another gave the record from one half hour to about four hours, and a third gave the record up to 24 hours With the guidance of the test results obtained, one of these calorimeters may be omitted in future work

The first calorimeter, for immediate heat liberation, was simply a Dewar jar fitted with a sensitive mercury thermometer passing through a thick cork Cement was placed in the jar and cold water of known weight and temperature was added and mixed with the cement Temperatures of the paste were observed at 3, 15, and 30 minutes The heat liberation was computed by comparing these temperatures with the initial temperatures of the materials, taking account of respective weights and specific heats This method was not reliable beyond about 30 minutes because the heat transfer became large in comparison with the slow heat liberation at this time

The intermediate calorimeter was also a Dewar jar, but prepared to take a paste specimen sealed in a bottle In order to equalize the paste temperature, a copper rod extended through the cork to the bottom of the bottle An electrical resistance thermometer mounted on the copper permitted temperature measurement to 0 03° C Conversion of temperature rise into heat units necessitated knowing the heat capacity of all materials in the jar With this calorimeter, measurements could be taken even after the paste had hardened, without damaging the thermometer unit

The final, "conduction" calorimeter, to extend results to 24 hours, was of a new design, similar in principle to the vane calorimeter [1] It permitted the instantaneous rate of heat liberation to be determined at approximately constant temperature Heat was conducted away from a specimen almost as fast as it was liberated The rate of conduction was determined by observing the small temperature difference between the ends of a metal tube along which the heat was conducted This temperature difference could be measured readily to about 0 02° C with resistance thermometers and a test set designed to measure difference directly (If many tests are to be made, a recorder can be obtained that will make a continuous record on as many as 6 calorimeters simultaneously) A cross section of the conduction calorimeter is shown in Figure 1 The figure indicates how the heat is taken from the specimen by a copper rod, how the opposite end of the metal tube is maintained at substantially constant temperature, and how a Dewar jar prevents heat loss except in the direction of the metal tube Credit for suggesting this modification of the vane calorimeter is due I L Tyler, concrete technician for the Tennessee Valley Authority

The water cement ratio for most of the tests was 0 35 by weight This value made as dry a paste as could be stirred readily for the early tests It was found that the water content of the paste, within ordinary limits, had only a slight effect on the early heat liberation

The temperature of the hydrating paste was approximately 70° F In the conduction calorimeter, high-early-strength cements rose in temperature as much as 15° F during the period of rapid hydration, but the average temperature for 24 hours was not much above 70° F Proposed improvements in the calorimeter will reduce the variations in curing temperature by about one half

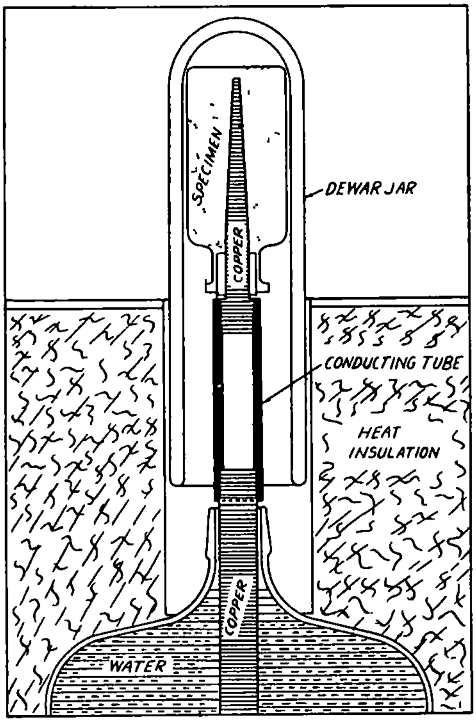

Figure 1 Conduction Calorimeter

[1] The Vane Calorimeter R W Carlson, *Proceedings* Am Soc T M 1933

GENERAL FINDINGS

Typical Heat Liberation of Hydrating Cement When water is first added to portland cement, there is an immediate heat liberation of appreciable amount

Only a small portion of the immediate heat is directly due to wetting the cement, the major portion is due to the dissolving of readily-soluble "impurities," such as free lime and probably alkalis This heat continues to be liberated for a number of minutes at a decreasing rate until, at about two hours, it is imperceptible

Before the "impurities" have ceased to liberate heat at a noticeable rate, the hydration of two of the major compounds, tricalcium aluminate and tricalcium silicate, begins to evolve heat at an increasing rate Thus, a minimum rate of heat generation, at about two hours, is followed by a maximum rate at about 8 hours The maximum is usually reached an hour or more after final set has been attained, and is followed by a gradual decrease in rate At the end of 24 hours, the rate is only a fraction of the maximum, and if tests are continued for several days, the rate is found to be only about one per cent of the maximum

Many exploratory tests were made to determine what differences in early heat liberation might be expected due to various causes Standard portland cements were found to vary widely among themselves The differences were magnified by plotting curves of the instantaneous rates of heat liberation, rather than cumulative heat of hydration A few such curves for selected standard cements are shown in Figure 2 Bearing in mind that these curves were all obtained on standard portland cements, the differences are striking One need not conclude that standard cements are necessarily of wide variation in quality, but rather that the early-heat curves are a sensitive index of the early hydration of the cement

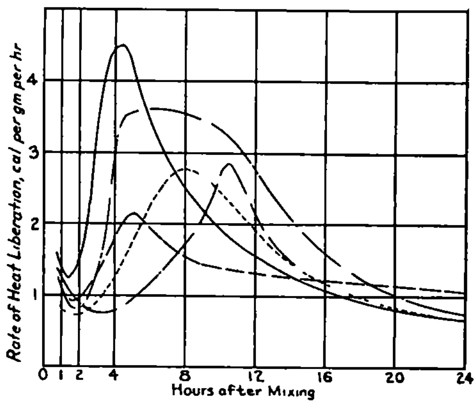

Figure 2 Early Heat Characteristics of Standard Cements

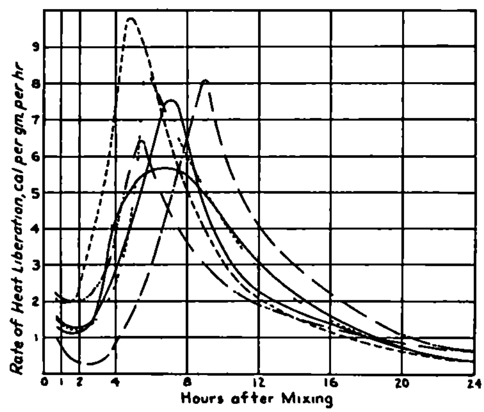

Figure 3 Early Heat Curves of High Early Strength Cements

Similarly, Figure 3 presents the early heat characteristics of selected high-early-strength cements Note that the maximum rates of heat liberation are much greater than those of standard cements Again, differences between cements are apparent

Even greater differences are exhibited by different types of cement In Figure 4 are shown selected heat curves for five types of cement standard, high early strength, modified, low heat, and portland puzzolan The particular cements selected were of nearly the same fineness, so the curves show in a general way the effect of composition The standard cement was one of low tricalcium aluminate content, otherwise its curve would differ less from those of the two high-early-strength cements included The low-heat and modified cements represented in Figure 4 were closely similar in composition

Now that curves have been presented showing the different early-heat characteristics of cements, the questions arise as to what their significance may be and how the characteristics may be varied The effect of a few factors on the early heat will first be discussed, and later the correlation of early heats with properties of cements will be attempted

The variables that were found to have a pronounced effect on the early rates of heat liberation were

1 Fineness of cement,
2 Chemical composition,
3 Amount and condition of retarder,
4 Rapidity of cooling of cement clinker,
5 Temperature of hydration,
6 "Conditioning" or ageing of cement, and
7 Admixtures and impurities

Most of these variables have not yet been studied thoroughly, but some discussion of the effect of each on heat of hydration will be given before attempting the correlation of heat of hydration with performance

Effect of Cement Fineness The effect of finer grinding of cement is to increase both the maximum rate and the total amount of heat liberated during the first day of hydration The shape of the heat-rate curve is not greatly affected The general effect can be seen by comparing the curves of Figure 2 with those of Figure 3, because a single clinker was used in making each of several pairs of the particular standard and high-early-strength cements included

Effect of Composition Nearly all of the heat liberated between 15 minutes and 24 hours after the mixing of cement with water is believed to be due to the hydration of only two compounds, tricalcium aluminate and tricalcium silicate The remaining compounds are believed to contribute little to the early heat The heat liberation of dicalcium silicate, for example, attains a maximum rate of only about 0 1 cal per gram per hour during the first day, even when ground quite fine Of the two compounds largely responsible for the early heat liberation, tricalcium aluminate hydrates the more rapidly and is responsible for the abnormally high and abrupt heat liberation that is observed in some cements It seems safe to say that the majority of the tricalcium

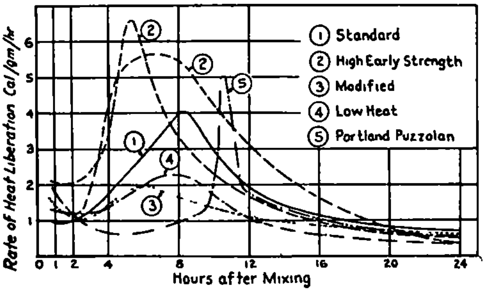

Figure 4 Early Heat Characteristics of Various Types of Cement

aluminate present in a fairly fine cement hydrates within 24 hours Since each one per cent of this compound has a potential heat liberation of 2 2 calories per gram of cement,[2] the proportion of the 24-hour heat attributable to tricalcium aluminate can be estimated Tricalcium silicate, being present in larger amount, may liberate more heat than the tricalcium aluminate, but at a more uniform rate

Effect of Gypsum · A standard-cement clinker was ground with different amounts of gypsum to make five cements of equal fineness but with SO_3 contents ranging from 0 5 to 2 5 per cent The early heat curves for these cements are presented in Figure 5

[2] Woods, Starke, and Steinour, "Heat Evolved by Cement During Hardening" Eng News-Record, Oct 6, 1932

The cement with only 0 5 per cent of SO_3 exhibited a flash set with the liberation of a considerable amount of heat, following which there were several hours of slow hydration The heat liberation then increased slowly and a low maximum was reached at about 15 hours

With 1 0 per cent of SO_3, the rate of heat liberation during the first few hours was normal (as with 1 5 per cent SO_3) but a maximum was reached at the early age of 5 hours as compared with about 8 hours normal for this cement The maximum rate was only about 60 per cent of normal but the rate at 24 hours

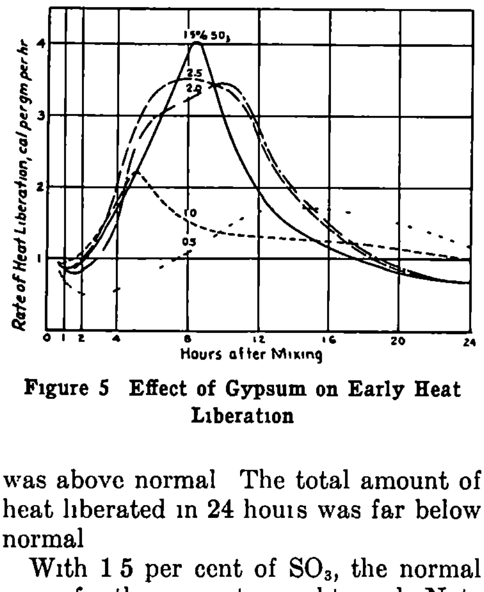

Figure 5 Effect of Gypsum on Early Heat Liberation

was above normal The total amount of heat liberated in 24 hours was far below normal

With 1 5 per cent of SO_3, the normal curve for this cement was obtained Note that the heat-rate curve is sharp and that the maximum rate of heat liberation is higher than for any other amount of SO_3 investigated

With 2 0 and 2 5 per cent of SO_3, the total heat liberation during the first 24 hours became progressively more extensive, but the greater liberation was attained through a prolonging of the period of rapid liberation and not by increasing the maximum rate

The effect of different forms of gypsum, such as plaster of paris and the "anhydride" forms, have not yet been investigated It would seem that the efficiency of the retarding action of various forms might be studied to advantage from the heat-of-hydration standpoint

Effect of Rate of Cooling of Cement Clinker Only a few tests were made with cements of different "glass" contents, such as result from different conditions of cooling of freshly-burned clinker It is indicated, however, that while the "glass" content has little effect on cements containing small amounts of potential tricalcium aluminate, it has a large effect where the computed percentage of tricalcium aluminate is high Due to the fact that preliminary tests were made on small specimens and therefore only qualitative, further tests are necessary before detailed comparisons can be presented

Effect of Temperature of Hydration The effect of raising the temperature of hydration was to increase both the maximum rate and the total amount of heat liberated up to 24 hours The time required to reach a maximum rate of heat liberation was materially reduced by raising the temperature An important effect of higher temperature appeared to be the reduced hydration at later ages, before 24 hours had elapsed, cements tested at elevated temperature were generating heat at a less rapid rate than were cements tested at normal temperature

Effect of "Conditioning" of Cement Two cements were treated with superheated steam so as to allow them to absorb a fraction of one per cent of moisture, according to the method developed and described by P S Roller[3] It was found that the maximum rates of heat liberation were materially reduced by the conditioning, although the total heat liberation up to 24 hours was not greatly

[3] Roller, Paul S, "Seasoning of Cement at Elevated Temperature," *Industrial Engineering and Chemistry*, Vol 28, March 1936

affected Further studies are planned on conditioned cements

Effect of Admixtures and Impurities Admixtures of certain kinds affect the heat-rate curves of hydrating cements, while many have no noticeable effect one portland-puzzolan cement that is more or less typical Note the high, but very sharp, maximum rate of heat liberation that occurred at about 10 hours The puzzolanic material was responsible for the sharp peak on the heat-rate curve

TABLE 1

COMPARISON OF SETTING TIME AND EARLY HEAT OF HYDRATION FOR VARIOUS CEMENTS

Cement symbol[1]	Normal consistency	Specific surface[2]	24-hour heat of hydration[3]	24-hour tensile strength[4]	Time required for			10 cal per gm[6]
					Initial set	4 cal per gm[5]	Final set	
AH	27 0	2280	61	335	2 10	3 10	4 40	4 40
AS	24 5	1570	43	150	2 00	2 50	4 00	4 20
BH-a	27 0	2390	69	300	1 50	2 00	3 50	3 30
BH-b	26 0	2360	60	290	2 10	2 15	4 10	3 40
CS	24 0	1670	30	105	4 45	4 15	9 30	9 00
DH	25 0	2010	58	330	3 45	3 10	6 00	5 10
EH	26 0	1930	64	290	2 10	2 45	5 25	5 10
FH	26 5	2390	62	295	5 25	5 00	7 30	7 00
GH	26 0	2170	59	320	2 50	3 30	5 35	5 30
HH	25 0	2250	53	280	1 45	2 00	4 15	4 15
JS-a		1740	30			(Fla	sh set)	
JS-b	24 5	1730	31	95	2 55	3 30	5 25	6 30
JS-c	24 0	1710	40	180	3 00	3 40	6 00	6 15
JS-d	24 0	1730	44	190	3 20	4 00	5 50	6 15
JS-e	24 0	1740	45	185	3 35	4 10	5 55	6 10
KP	29 0		26		3 45	3 30	8 45	10 00
LL	23 0		25		3 20	3 40	6 50	6 55
MM	23 0		26		3 50	3 40	6 35	6 50

Notes

1 Second letter signifies type of cement (H, high-early strength, S, standard, P, puzzolan, L, low-heat, and M, modified)

2 Square centimeters per gram as determined by Klein turbidimeter

3 Calories per gram, exclusive of first ½ hour

4 Pounds per square inch on standard mortar

5 Exclusive of first ½ hour

6 Exclusive of first ½ hour

Accelerating agents and retarding agents, including retarders other than gypsum, have especially large effects, while many common chemicals have little effect

Puzzolanic materials interground with cement altered the heat-rate curves, while the same materials simply mixed with cement had little effect Only puzzolanic materials that were reactive with lime, however, had a noticeable effect when interground with cement In Figure 4 there is included the curve of

RELATION BETWEEN HEAT CHARACTERISTICS AND PERFORMANCE OF CEMENT

Setting Times and Heat of Hydration After examining the cumulative heat curves of a number of cements, it appeared that initial set usually was reached when about 4 calories per gram had been liberated Similarly, final set usually corresponded to 10 calories per gram The immediate heat of hydration seemed to have no bearing on the setting times

In Table 1 are presented the measured setting times of a number of cements, and the corresponding times required for the heat of hydration to reach 4 and 10 calories per gram, respectively It may be noted that there is fair agreement between corresponding times In view of the fact that setting times are defined as

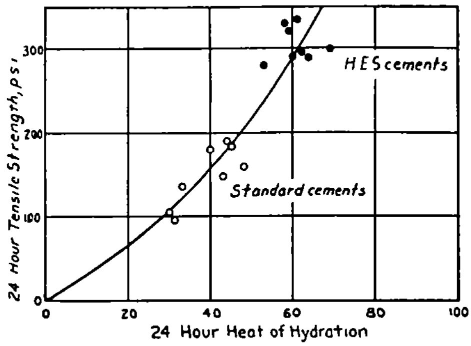

Figure 6 Relation Between Early Strength and Heat

the times required for arbitrary degrees of hardness and that they are not easily reproducible, the agreement is as good as could be expected Actually, the final set can probably be determined to a greater degree of reproducibility by heat measurements than by the usual method for determining final set The initial set is less definitely related to the heat measurement, because of the difficulty of separating immediate heat from the heat liberated by the hydration of cementing compounds

24-Hour Strength and Heat of Hydration The one-day tensile strength of standard mortar was compared with the one-day heat liberation for a number of cements from different plants A plot of the results is shown in Figure 6 and the data are also included in Table 1 It may be noted that the relation between heat liberation and strength is reasonably good, despite the fact that compositions and manufacturing methods were different The fact that the strength does not seem to be directly proportional to the heat liberation may be due to the somewhat different curing temperatures and water cement ratios of specimens for heat and strength tests, respectively

Strength results on the cements containing different amounts of gypsum are included in Table 1 Note that the increase in gypsum content has a large effect in increasing the strength and heat in the lower range (up to 1 5 per cent), but that further increase has little effect It is believed that, except for experimental error, the 2 5 per cent SO_3 should show slightly higher strength than 2 0 per cent because it shows more heat of hydration Here, again, the heat measurement is believed to be the more accurate means of determining relative values

Bleeding of Concrete and Heat of Hydration While no quantitative studies have yet been made on the relation between bleeding of concrete and heat of hydration, some connection has been observed In some cases, those cements that exhibited unusually low rates of heat evolution after the immediate heat had subsided, were observed to bleed freely An early gelation seems to be necessary to prevent bleeding No definite conclusions are warranted, however, on the connection between bleeding and early heat liberation, until test data are available

Temperature Rise of Concrete Slabs The opinion has often been expressed that temperature rise of thin concrete slabs due to heat of hydration is not a factor worthy of consideration The present discussion is not intended to magnify the importance of heat generation in thin slabs, but rather to evaluate the importance without distortion In view of the fact that pavements cast with rapid-hardening cements but protected from drying, have been observed to crack due to temperature drop well within 24 hours, the heat of hydration would seem to be a factor in summer concreting

The manner in which heat of hydration may cause cracking should be borne in mind While the temperature is rising, the concrete is soft and plastic When maximum temperature is reached the concrete is under almost no stress but has attained a fair degree of rigidity and has lost much of its ability to deform plastically As the temperature then drops, tension tends to develop in a slab of considerable length, because contraction is prevented If a temperature drop of 15 or 20 degree occurs quickly, the concrete may crack

An important fact is that even though a greater temperature is attained during subsequent hot seasons than is attained during early hardening, the maximum temperature during early hardening is the reference temperature Drying shrinkage and temperature drop from this reference temperature determine the net tendency of the slab to contract

Without forgetting that seasonal variations in temperature and drying shrinkage are likely to be larger factors, a specific example of the effect of heat generation is illustrated by the curves of Figure 7 The curves show the computed temperatures, for each of three classes of cement, in 10-inch slabs with one face insulated and the other maintained at uniform temperature A cement content of 1 5 bbl per cu yd of concrete was assumed The curves are therefore only applicable to this single set of assumed conditions and should not be construed as being general

The curves of Figure 7 show that in a 10-inch slab containing rapid-hardening cement a substantial temperature rise of over 30° F may occur Not every high-early strength cement would produce such a high temperature rise, a cement that was above average in abruptness of early heat liberation was selected for illustration On the other hand, still higher temperatures would be exhibited by a few cements The temperature rises shown for modified and low heat cements are

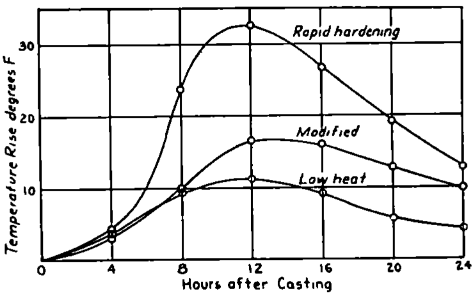

Figure 7 Effect of Cement on Temperature Rise in 10-In Slab

small enough to justify the conclusion that when they are used, heat generation is likely to be a small factor

CONCLUDING REMARKS

The test results and this discussion must be considered as preliminary and therefore no conclusions are drawn Cement research employing calorimetric methods will be continued in the hope of having more accurate and useful results to report in the future It is only hoped that this paper may help to give a better understanding of the early hydration of cement