PHOTOGRAPH THIS SHEET

ADA950196

DTIC ACCESSION NUMBER

LEVEL

INVENTORY

AEWES Tech Memo. 6-410

DOCUMENT IDENTIFICATION

July 55

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DISTRIBUTION STATEMENT

| ACCESSION FOR | |
|---|---|
| NTIS GRA&I | ☒ |
| DTIC TAB | ☐ |
| UNANNOUNCED | ☐ |
| JUSTIFICATION (July 1955) | |
| BY Per DTIC Form 50 on file | |
| DISTRIBUTION / | |
| AVAILABILITY CODES | |
| DIST | AVAIL AND/OR SPECIAL |
| A | |

DISTRIBUTION STAMP

Released

DTIC
ELECTE
MAR 30 1981
S D
D

DATE ACCESSIONED

UNANNOUNCED

81 3 27 54

DATE RECEIVED IN DTIC

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-DDA-2

DTIC FORM OCT 79 70A

DOCUMENT PROCESSING SHEET

CORPS OF ENGINEERS, U. S. ARMY

# HEAT OF HYDRATION OF BLENDS OF A PORTLAND AND A NATURAL CEMENT

CWI ITEM NO. 601

RESEARCH IN MASS CONCRETE

TECHNICAL MEMORANDUM NO. 6-410

CONDUCTED FOR

OFFICE OF THE CHIEF OF ENGINEERS

BY

WATERWAYS EXPERIMENT STATION

VICKSBURG, MISSISSIPPI

ARMY-MRC VICKSBURG, MISS.

JULY 1955

THE CONTENTS OF THIS REPORT ARE NOT TO BE USED
FOR ADVERTISING, PUBLICATION, OR PROMOTIONAL
PURPOSES

# PREFACE

The tests reported herein form a part of CWI Item No. 601, "Research in Mass Concrete," an item of the Civil Works Investigations program of the Office, Chief of Engineers. The work was done at the Concrete Division of the Waterways Experiment Station under the supervision of Messrs. Herbert K. Cook and Bryant Mather. Mr. Leonard Pepper, Chief, Chemistry Section, assisted by Mr. E. J. Calian and other members of the staff, performed the tests and prepared the report.

CONTENTS

## SYNOPSIS

Replacement of part of the portland cement in concrete by a material of lower chemical activity should reduce the heat evolution and temperature rise of the concrete. Quantitative measurements are required to determine whether the heats of hydration of portland cement and another material are additive when blended and whether total heat is predictable from tests of the component materials. Methods for such measurements are needed.

This investigation involved a study of three methods of determining heat of hydration of blends of a portland and a natural cement. Two of the methods, heat-of-solution and conduction-calorimeter, have been developed to the extent that they may be used in routine studies of such materials.

The investigation indicated that the heats of hydration of portland and natural cement are not additive when blended and that total heat cannot be predicted from tests of the individual components.

# HEAT OF HYDRATION OF BLENDS OF A PORTLAND AND A NATURAL CEMENT

## PART I: INTRODUCTION AND SCOPE

### Heat Evolution

#### Effects of heat evolution

1. The reduction of the amount of heat evolved in mass concrete is of considerable importance since such reduction lowers the temperature rise and hence materially lessens the tendency of concrete to crack on cooling. The reduction of cracking is of prime importance in minimizing the passage of water through the concrete, in reducing the expense of repairs, and in preserving the appearance of the concrete surfaces.

#### Methods of reducing heat evolution

2. The amount of heat evolved depends both on the amount of cementitious material in the concrete mixture and upon the heat of hydration of that material. Consequently, the amount of heat may be reduced by either or all of the following means: (a) reduction of the cement content of the concrete, (b) substitution of some cementitious material of lower heat of hydration for part of the portland cement, or (c) use of portland cement manufactured to have low heat of hydration.

### Scope of This Investigation

3. Studies[2,3]* conducted by the Corps of Engineers on blends of portland and natural cements prior to the present investigation did not include the determination of heats of hydration of these blends. The interpretation of temperature-rise test data obtained for concrete containing such blends requires knowledge of the heat of hydration. This

---

* Raised numerals refer to similarly numbered entries in the references cited at the end of this text.

report covers the results of an investigation of the heats of hydration of various blends of a portland and a natural cement and includes an evaluation of several methods of making such studies.* This work also served to point to and develop improved means of applying standard procedures to these slowly reacting materials. Several methods for determining heats of hydration were used in this study and modified as needed. A comparison of results obtained together with a limited discussion of the relative merits of these methods is given herein.

---

* On the basis of some of the preliminary results obtained in this investigation, the heats of hydration of commercially available materials and blends of some of these materials with portland cement were subsequently studied. The results of these studies have been published[5,6].

# PART II: MATERIALS AND METHODS

## Materials

4. Two cements were used in this program, a Type II portland cement designated RC-184, and a natural cement designated RC-161. The results of chemical analyses of both cements are shown in table 1. All the tests described below were made on each of the following blends of these two cements:

| Blend | Composition Per Cent by Absolute Volume — Portland | | Natural |
|---|---|---|---|
| A | 100% RC-184 | | ----------- |
| B | 75% RC-184 | + | 25% RC-161 |
| C | 65% RC-184 | + | 35% RC-161 |
| D | 50% RC-184 | + | 50% RC-161 |
| E | ----------- | | 100% RC-161 |

The specific gravities were taken as 3.15 for the portland cement and 2.90 for the natural cement. All pastes were mixed to a water-cement ratio of 0.40 by weight.

## Methods

5. Three different test methods were used for the determination of the heats of hydration of the cements and blends. Two of the methods, the twin-calorimeter and conduction-calorimeter, are similar in that they are both continuous heat evolution methods. At the time this study was initiated, the Waterways Experiment Station had had no experience with continuous heat evolution determinations of cement pastes and there were but few references to either method in the available literature[1,7]. It was believed, however, that the rate of heat evolution at various ages, as determined by a continuous heat evolution method, would be a better criterion for comparing various cements and cement blends than the total heat of hydration at various ages. Therefore, it seemed desirable to develop a suitable continuous heat evolution test method.

The third test method contemplated was the heat-of-solution method for the determination of the total heat of hydration at various ages. This test method is standard for portland cements, but changes in the method were necessary to test slowly reacting materials.

## Heat-of-solution Method

### Standard method

6. The procedure for determination of the heat of hydration of portland cement pastes by the heat-of-solution method is fully described in CRD-C 201-52 and CRD-C 229-48[4] (Federal Specifications SS-C-158c, par 4.4.10 and ASTM Designation C 186-47). The heat of hydration, as determined by this method, is the difference between the heats of solution of the dry, unhydrated cement and the partially hydrated paste. The heats of solution are obtained from the heat rise in the calorimeter as a result of dissolution of the material in a dilute solution of nitric and hydrofluoric acids, and from a prior determination of the heat capacity of the system. A number of correction factors are applied to the calculations owing to the differences in temperatures between the materials and the differences in temperatures between determinations. The major errors in the determination are due to the carbonation and to the loss of moisture from the paste; both occur during the process of grinding the paste to pass a No. 20 sieve. The grinding process is essential to insure complete solution of the material within thirty minutes. Solution periods in excess of thirty minutes would increase the temperature correction factors and thereby introduce other major uncontrollable errors.

### Modifications to the method

7. The above procedure cannot be applied directly to slowly reacting cementitious materials, since pastes made from these materials cannot be completely dissolved within thirty minutes. The procedure may be altered in any one of three ways[8], as follows:

a. The concentration of the hydrofluoric acid in the acid solution may be increased to such an extent that the material will go completely into solution within thirty minutes. This modification will change the heat capacity of the system, and the change will be directly related to the number of milliliters of hydrofluoric acid added.

b. The solution period, using the normal concentration of the acids, may be arbitrarily extended for some definite time interval beyond thirty minutes. This interval must be followed by an apparent final rating period.

c. The solution period may be arbitrarily terminated at the end of thirty minutes. If the leakage constant of the calorimeter is assumed to be the same as that obtained for portland cements, the calculations may be based upon the preliminary rating period and the final rating period need not be determined.

Procedure used in this work

8. Modification a was tried unsuccessfully in the determination of the heat of solution of the natural cement. The volume of hydrofluoric acid was increased stepwise up to 100 ml, and the solution period still exceeded thirty minutes. It was found, however, that the leakage constant averaged 0.0045 for portland-cement determinations if the room temperature and the temperature rise in the calorimeter remained fairly constant. Both modifications b and c assume that the amount of material that dissolves is dependent only upon the time the material is in contact with the acid. Therefore, the heat of solution of pastes at any age may be compared with the heat of solution of the dry material. Since the temperature corrections are smaller for the thirty-minute solution period, modification c was used for the determinations of the heats of solution of the natural cement and blends made using it. The heat of solution of the portland cement was determined using the standard method. The procedure and calculations are illustrated in the data presented in tables 2 and 3.

## Specific Heat and Immediate Heat of Hydration

Continuous heat evolution

9. The continuous heat evolution method requires the determination of the heat evolved from a system as it is liberated, or, as is done in practice, at very short time intervals. For isothermal systems, the heat evolved is determined from the minute temperature differences between the

system and its surroundings, or from the temperature increase of the surroundings of the system. For adiabatic systems, the heat evolved is determined from the temperature increase of the system and the knowledge of its specific heat. However, it is very difficult, if not impossible, to obtain either a true isothermal or true adiabatic system. There will always be a temperature rise, or heat storage, in the system and some heat lost to the surroundings. It was therefore necessary to determine the specific heats not only for the dry cements and blends but also for the pastes made from the cements and blends at various ages. In addition, it did not prove feasible to determine the heat evolved from the moment the cement and water are mixed together. Therefore, it was necessary to determine the "immediate heat of hydration" by other means.

Procedure for deter-
mination of specific heat

10. The method of mixtures is one of the simplest methods available for the determination of specific heats of materials and if used with proper precautions will produce results having a fair degree of precision. The procedure developed and used for this program has been published as Method CRD-C 242-51 in the Handbook for Concrete and Cement[4]. The apparatus used, except for some minor changes and additions, is identical with the apparatus used for the determination of heat of solution. Artificial sapphire and standard Ottawa sand are used as specific heat standards and kerosene is used as the liquid medium for cement and pastes. The water equivalent of the system is first determined using the artificial sapphire and water. The specific heat of kerosene may then be determined by repeating the run, substituting kerosene for water. Both determinations should then be verified by repeating the determination using standard Ottawa sand and kerosene. It has been found possible to obtain specific heats with a standard deviation of 0.003 or better when the following conditions are adhered to:

a. The volume of the material within the calorimeter must be relatively constant.

b. The temperature change within the calorimeter must be at least one degree centigrade.

c. The addition of material to the calorimeter must be completed within 0.4 min.

d. The liquid medium must cover the mercury well of the differential thermometer.

Typical specific heat data and calculations are shown in tables 4 and 5.

Procedure for determination of immediate heat

11. The heat liberated before the first measurement can be made with a continuous heat evolution calorimeter must be determined by an independent method since cements liberate an appreciable amount of heat immediately upon being mixed with water. The heat liberated during this initial period is referred to as the immediate heat of hydration. It is determined with a Dewar flask identical with those used for the determination of specific heats and heats of solution. Three hundred grams of cement and 120 ml of water are used for the determination. The initial temperature of the water is adjusted in such manner that the paste at the completion of a determination will be approximately at room temperature. The measured quantity of water is placed in the flask and the initial temperatures of the water and cement are recorded. The cement is then poured into the flask, the stopper and thermometer inserted, and the contents shaken or stirred vigorously for 5 min. Readings of the paste temperature are taken at 5-min intervals for 30 min. The heat of hydration is then calculated from the temperature rise and the heat capacity of the system (cement, water, and flask). Typical data and calculations are shown in table 6.

## Twin-calorimeter Method

Sample preparation

12. The twin-calorimeter method of determining continuous heat evolution approaches an adiabatic system. The calorimeters are well-insulated Dewar flasks of 1-qt capacity. It is assumed that both flasks have identical heat capacities. Since mechanical stirring of the paste will cause a temperature rise of approximately 10 C, the paste, composed

of 120 g of water and 300 g of cement at room temperature, is well-stirred by hand for at least 5 min. The paste is poured into a tared 250-ml Erlenmeyer flask and into two vials. The vials are sealed and, upon completion of the run, are used for determination of ignition loss. After the weight of the paste added to the flask has been determined, two thermocouples are inserted in the paste, and the flask is stoppered and sealed. A quantity of water is added to a second 250-ml flask so that the heat capacity of the water is approximately equal to the heat capacity of the paste. Two thermocouples and a heater are inserted in the water and that flask is stoppered and sealed.

Thermocouple connections

13. One thermocouple from each flask is connected to a recording potentiometer. The other thermocouple is connected to a differential controller. The controller consists essentially of a null-balanced voltage bridge. When the temperature of the water is below that of the paste, the automatic balancing action of the bridge will actuate a mercury switch, which in turn will close a circuit consisting of a 115-v, a-c source, a watt-hour meter, and the heater which is placed in the water. When the water temperature is greater than the paste temperature, the mercury switch opens the circuit. The temperature will not vary more than ± 0.1 F, which is the limit of accuracy of the temperature recorder.

The twin-calorimeter heater

14. The heater consists of a 6-w, 115-v, a-c light bulb with all electrical contacts heavily sealed with sealing wax. To insure against electrical short circuits which may be caused by water vapor, the bulb is placed in a glass vial of such length that the bulb extends below the surface of the water and the upper part of the vial is within the cork used to stopper the flask. The vial is sealed with sealing wax. Since the current used by the 6-w bulb is small and will not actuate the watt-hour meter when the power is on for very short time intervals, a 300-w bulb is put in series with the 6-w bulb. The power consumed by the bulbs should be determined for various voltages so that the power used by the 6-w bulb during the determination may be calculated from the watt-hour readings.

Power readings

15. After all connections are made, each flask is put into the proper calorimeter. Glass wool is wrapped around each flask for additional heat insulation and the calorimeters are then covered with a lucite cylinder. The first reading of the temperatures, the power used, and the line voltage is taken half an hour after the water is added to the cement. Readings are taken every half-hour at the beginning of the determination. As the rate of hydration decreases, readings may be taken every hour, then every two, four, and eight hours. After a paste age of 3 days is attained, readings need only be taken every 12 or 24 hours. Since the power used is not recorded automatically and continuously as are the temperature readings, the power consumed in any time interval can only be obtained by interpolation.

Calculations

16. Calculations of the rate of heat liberated and the heat of hydration are made assuming that the heat lost by the calorimeter containing the paste is the same as the heat lost by the calorimeter containing the water. For any time interval, the temperature loss of the paste and the water is obtained by the algebraic subtraction of the actual temperature rise (or fall) of the water from the temperature rise the water would have undergone if there had been no heat loss (obtained as a product of the heat capacity of the water and the power consumed by the water for that time interval). The corrected temperature rise of the paste for any time interval would then be the algebraic sum of the actual temperature rise of the paste for any time interval and the temperature loss of the paste for the same time interval. The product of the calculated temperature rise and the heat capacity of the paste (for the conditions of the time interval) is the heat of hydration for the time interval. Dividing the above product by the number of hours in the time interval will give the rate of heat liberation. The heat capacity of the paste is calculated on the ignited-weight basis. Typical data and calculations are illustrated in table 7.

## Conduction-calorimeter Method

### Description of the calorimeter

17. The conduction-calorimeter method of determining the continuous heat evolution approaches an isothermal system. The heat, as it develops in the specimen, is conducted down a brass or copper cylinder to a series of copper vanes where it is dissipated in a water bath. However, when the heat development is rapid, as it is for the first 8 to 24 hours, some of the heat will be stored in the sample and the temperature of the specimen will be increased. To reduce or prevent heat losses to other parts of the system by radiation or convection, the specimen and the conduction cylinder are covered with a Dewar flask and then completely enclosed within an adequately insulated box.

### Resistance coils

18. The heat evolved from the isothermal system is determined by measurement of the temperature differences between the system and its surroundings; in this case, the specimen and the water bath. Two resistance coils, having a resistance of approximately 50 ohms, are used to measure the temperature difference. One coil, having a slightly higher resistance than the other, is placed on the upper part of the cylinder, just below the copper specimen cup. The other coil is placed on the lower part of the cylinder just above the copper vanes which are completely submerged in the water bath. The two resistance coils are interconnected so that resistance difference is measured. The coil leads, which should be of very low resistance, are connected to a Wheatstone bridge and a recorder, both being capable of detecting and recording a resistance difference of 0.005 ohm.

### Calibration

19. The calorimeter is calibrated electrically so that the recorder readings can be converted to both the rate of heat liberation (calories per second) and the temperature difference between the specimen and the water. A heater, which may be a resistance coil, and a thermocouple are placed in the specimen cup. A second thermocouple is placed in the water bath below the calorimeter and in the center of the radiating copper

vanes. Both thermocouples are connected to a K-type or similar potentiometer. The heater is powered by a storage battery having in its circuit a voltmeter, ammeter, and a rheostat. Temperature readings are taken, and the power consumed by the heater is determined when the recorder reaches an equilibrium value. At least five calibration points should be obtained by varying the voltage.

Temperature regulation

20. After the initial release of heat, i.e., after 24 hours, the temperature difference between the specimen and the water will become very small. Fluctuations in the temperatures of the room and the water will, therefore, be of importance and should be controlled as closely as possible. The room temperature variation should be not more than 2 F. The water should be slowly circulated both to insure removal of the heated water from around the calorimeter vanes and to decrease the temperature fluctuation of the water. The apparatus constructed by the Waterways Experiment Station has been found to give satisfactory results up to a paste age of 7 days. For determinations of comparable accuracy at later paste ages, the water temperature would have to be more closely controlled and a more sensitive bridge and recorder would be necessary.

Sample preparation

21. The determinations using the conduction calorimeter and the twin calorimeter require similar procedures. Three hundred grams of cement and 120 grams of water are well mixed together for 5 min. Whether the paste is mixed by hand or mechanical means, it is important to have the final paste temperature very close to the calorimeter water bath temperature. Therefore, in this investigation the mixing water was cooled to about 5 C and the final paste temperature was adjusted to be approximately equal to the temperature of the calorimeter water bath by either cooling or heating the paste as needed. The paste is placed in a tared copper specimen cup and in two vials. The vials are sealed and used for determination of ignition loss upon completion of the run. The copper specimen cup should be greased before the paste is added to facilitate removal of the hardened paste at the end of the test. After the paste is added to the cup it is sealed with a lucite plug and

weighed. The cup is then placed on the conduction cylinder and the vacuum flask is placed over both cup and cylinder.

Calculations

22. Readings of the resistance difference between the two resistance coils are taken one-half hour after the water is added and every 15 min thereafter until the rate of heat liberation becomes rather small for this time interval. As the rate decreases, readings may be taken every half-hour, hour, two hours, etc. After a paste age of 3 days is attained, readings need only be taken every 12 or 24 hours. The average recorder readings of resistance-difference for any time interval are converted by means of the calibration constant to the heat liberated in calories per second. The recorder readings at the start and end of any time interval are converted to the temperature change of the paste. The total heat liberated in any time interval will be the algebraic sum of the product of the heat liberated (cal per sec) and the time length of the period (sec), and the product of the temperature change of the paste during the period (C) and the heat capacity of the paste at that age (cal per C). The ignited weight of the paste is used to convert the heat liberated to calories per gram. Typical data and calculations are shown in table 8.

# PART III: DISCUSSION OF RESULTS

## Heat-of-solution Method

### Test results

23. Replacement of portland cement by natural cement did not proportionally reduce the heat of hydration. The results obtained by the heat-of-solution method for the blends were higher than expected; the heat-of-hydration values for Blend B (25 per cent natural and 75 per cent portland cement) were greater than those obtained for pastes made from portland cement alone, up to and including a paste age of 14 days. Therefore, these data suggest that heat of hydration is not an additive function for these two cements, and there apparently is some chemical reaction between them during hydration. Examination of the data in table 9 indicates that the reaction has its greatest influence on the heat of hydration at the paste age of 7 days, the influence is less, but about equal, for paste ages of 3 and 14 days, and is least at 28 days. The curve shown on fig. 1 for 100 per cent portland cement may be considered typical for a Type II cement under the conditions of the test; the heat of hydration rises sharply to 7 days and then increases at a slower rate. The results for natural cement alone indicate a sharp rise in heat of hydration prior to the 3-day determination. The slope of the natural cement curve between 3 and 28 days is approximately equal to the slope of the portland-cement curve between 7 and 28 days. The blends made from these cements produce curves that resemble the portland-cement curve.

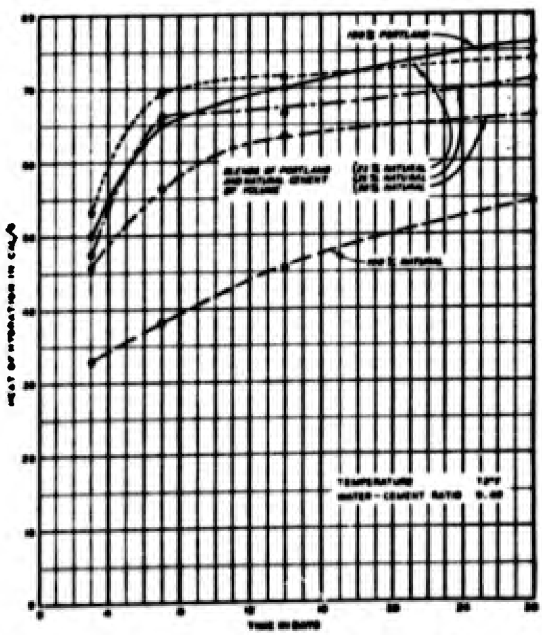


Fig. 1. Heat of hydration determined by heat-of-solution method

This is particularly true for the blends containing 25 and 35 per cent natural cement, in that there is a sharp rise to 7 days (the slope of the rise is greater than was found for portland cement) and then a flattening out to 28 days (the slope is less than for portland cement). The curve produced by the blend containing 50 per cent natural cement shows a rise to the 14-day paste age and then flattens out.

Precision of heat-of-solution determination

24. The deviation between duplicate determinations of the heat of solution of the blends and of the natural cement exceeded, in some instances, one calorie. This was to be expected because the degree of solution may not be identical (see paragraph 8) and because of the errors introduced by the grinding process (see paragraph 6). To check the effects of the grinding process, the water-cement ratios of the materials tested were calculated. The averages for each test are presented in table 10. The water-cement ratios were calculated from the difference between the reciprocal of the ignition ratio of the paste and the dry material. Although extreme caution was exercised during the grinding process in an attempt to keep conditions identical, it should be noted that the ratios differed between test ages and differed from the original ratio to which the material was mixed. It should also be noted that these calculated ratios increased as the percentage of natural cement in the material increased. Another source of error was eliminated by making more than one determination of the rate of temperature change in the preliminary rating period (see table 2). This was made necessary because of the elimination of the final rating periods in these determinations.

## Specific Heat and Immediate Heat of Hydration

Specific heat

25. The specific heat of both cement and pastes made from the cement was found to be, unlike the heat of hydration, an additive function. As the percentage of the natural cement in the blend increased, the specific heat of the material increased proportionally (see table 11).

The chemical reaction between the portland and the natural cement that affected the heat of hydration, making it a nonlinear function, did not affect the specific heat nor the physical state of the material. The over-all change in specific heat with time was found to be approximately 0.10 calories per gram of paste per degree centigrade at the end of 7 days, as indicated both by the data presented in table 11 and the curves shown on fig. 2. About 50 per cent of the reduction in specific heat due to time occurs within one hour after the cement is mixed with water. After 24 hours about 75 per cent of the change has occurred. There is a marked difference in the specific heat change with age of paste in portland and natural cements. Portland cement forms a smooth curve between 1 hour and 7 days, whereas the curve for natural cement is almost linear between 1 and 7 days. The blends made from these cements have curves that include characteristics of both ingredients.

Precision of specific heat test results

26. The deviations between results in determination of specific

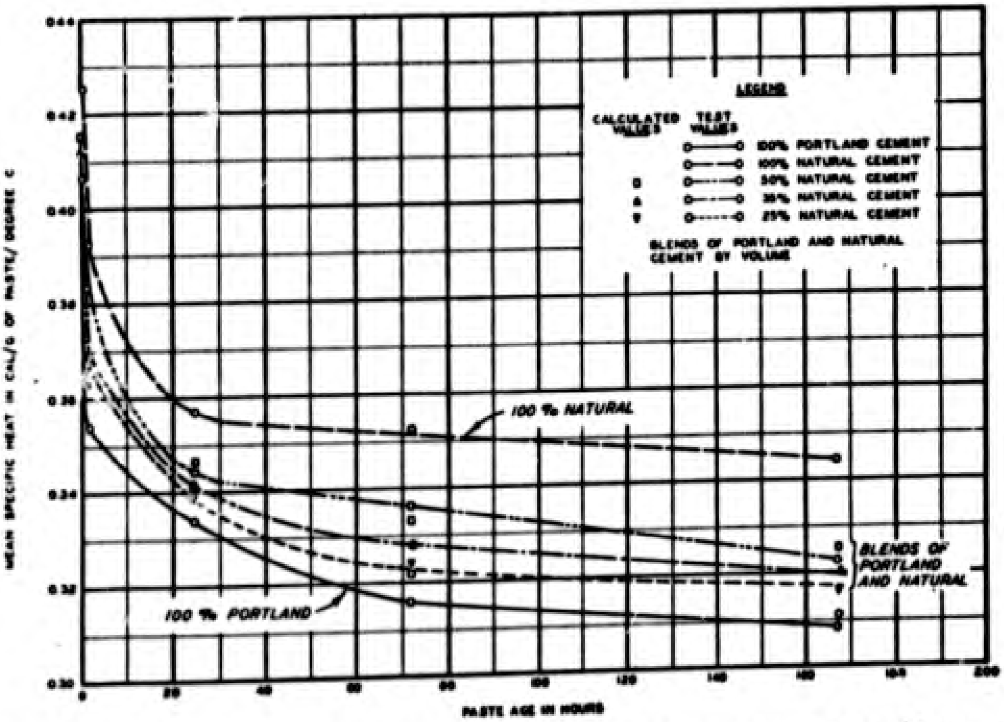



Fig. 2. Mean specific heat of pastes at room temperature at various ages

heat varied somewhat, and the errors encountered were similar to those encountered in the heat-of-solution method. Temperature fluctuations and the handling of moist materials (at times liquid) produced the most serious errors. Experience and good technique should reduce these to a permissible magnitude. One-hour pastes required special handling, since they were still fluid. A technique found to be successful, and finally adopted, involved vibrating the paste from a glass vial into the calorimeter, using the chuck which holds the stirring rod as the vibrator. The vial, held vertically with the open end pointed down, is pressed against the rotating chuck. The resulting vibrations cause the fluid paste to flow into the calorimeter.

Immediate heat-of-
<u>hydration test results</u>

27. The data obtained for the immediate heat of hydration and the rate of heat liberation at early ages are presented in table 12. It is not surprising to find that the immediate heat of hydration is not an additive function. However, the total heat released within thirty minutes was the same for both the portland and natural cements. The total heat released by the blends was somewhat higher. The rate of heat liberation was found to be quite different for portland and natural cements (see fig. 3). Portland cement rose to a peak in the first five minutes and then fell off rapidly. Natural cement had two peaks -- the first occurred within the first five minutes and was about 60 per cent of the magnitude of the portland-cement peak; the second occurred between ten and fifteen minutes and was about 40 per

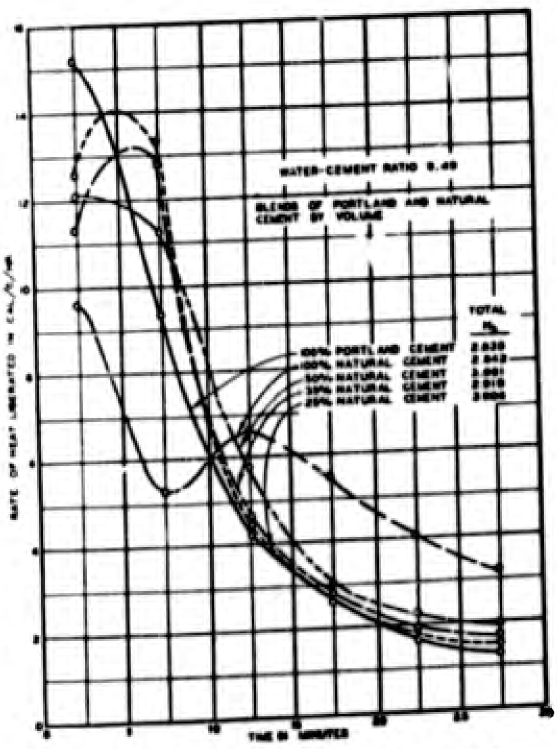



Fig. 3. Rate of immediate heat liberation of pastes

cent of the magnitude of the portland-cement peak. The effects of replacing portland with natural cement were to broaden and reduce the peak, and to increase the final rate (between 25 and 30 minutes) proportionally with the increase of natural cement. This determination, since it does not involve any special sample preparation or as many prior calibrations, is not subject to as many uncontrollable errors as is the determination of the heat of solution or specific heat. It is important, however, to subject each sample to vigorous stirring or shaking during the first five minutes to insure sharp peaks in the rate of heat liberation curve. In addition, an "equal" amount of stirring or shaking will be necessary to obtain reproducible rate-of-heat-liberation results.

## Twin-calorimeter Method

### Heat-of-hydration test results

28. The results obtained with the twin calorimeter are tabulated in table 13 and plotted on figs. 4 and 5. The heat of hydration as

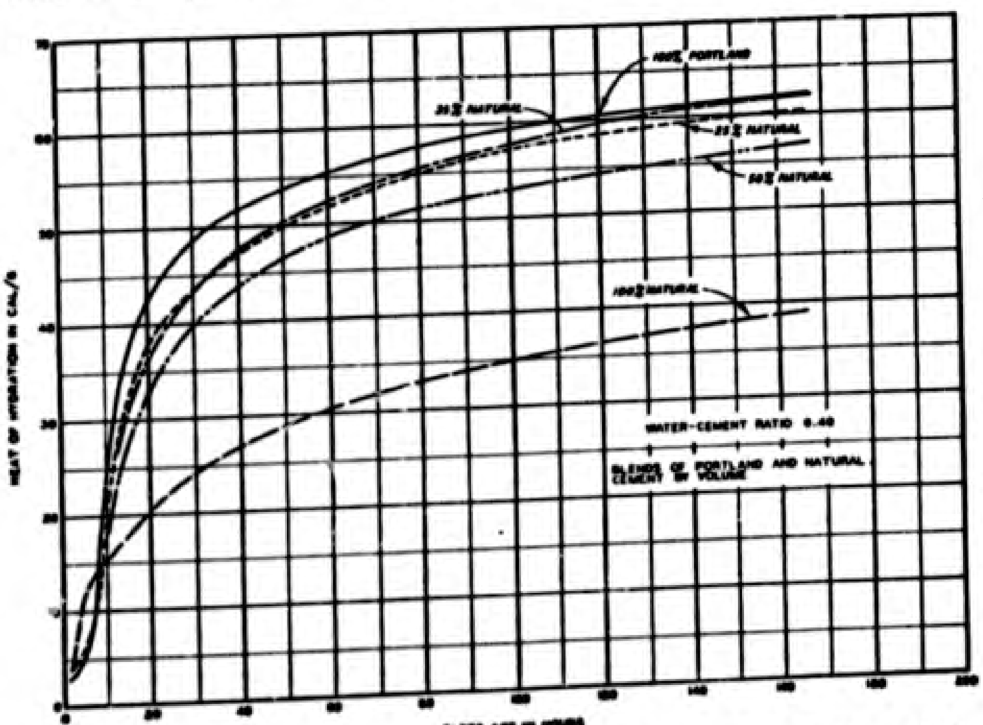



Fig. 4. Heat of hydration determined by twin-calorimeter method

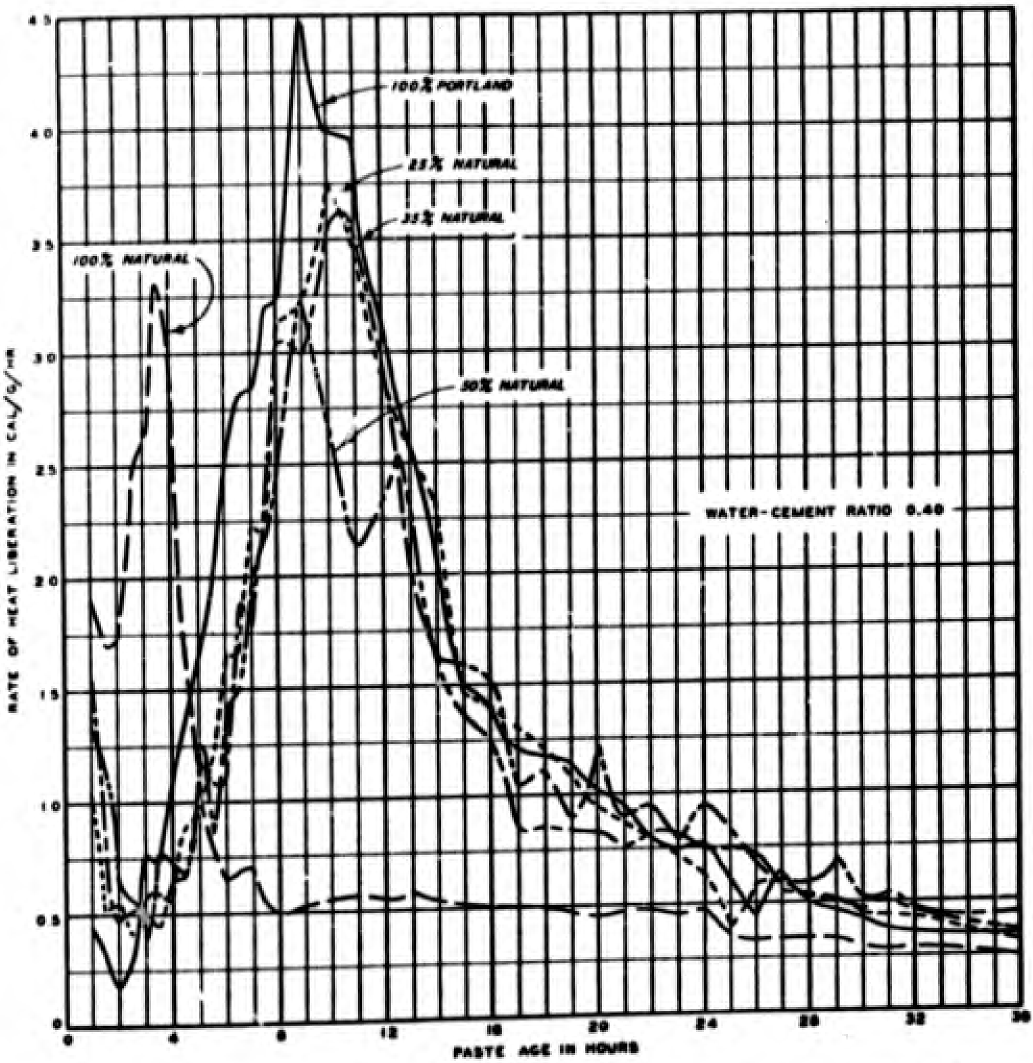



Fig. 5. Rate of heat liberation, twin-calorimeter method

determined by this method, since it involves an approach to an adiabatic system, rises rapidly at early ages. Sixty to seventy-five per cent of the 7-day value is attained at the end of one day; 90 per cent of 7-day value is reached at the end of three days. Here, too, it should also be noted that the heat of hydration is not additive; however, the values attained for portland cement are at all times greater, for the length of the test, than those of any of the blends. The blends containing 25 and 35 per cent natural cement come within 1.5 calories of the portland-cement value at 7 days.

Rate-of-heat-liberation test results

29. The rates of heat liberation for these blends are shown on fig. 5. The maximum rate of heat liberation occurs, for all the blends with the exception of the 100 per cent natural cement, between 9 and 11 hours; the natural-cement peak occurs between 3 and 4 hours. In general, the blends fall within the envelope of portland cement, and the peaks, with reference to portland cement, move somewhat to the right as the blends become richer in natural cement until blend containing 50 per cent natural cement is reached, where two peaks are found. The larger peak occurs at an age of between 8 and 9 hours and the smaller between 12 and 13 hours. The rate curves, on the whole, are not as smooth as was expected which might be due to insufficient initial stirring of the paste.

## Conduction-calorimeter Method

Heat-of-hydration test results

30. The results obtained with the conduction calorimeter are tabulated in table 14 and plotted on figs. 6 and 7. The heat of hydration as determined by this method rises less rapidly than when determined by the twin-calorimeter method. Fifty-five to sixty per cent of the 7-day value is attained at the end of one day; 80 per cent of the 7-day value is reached at the end of the third day. Here, too, the heat of hydration is not additive, and the values attained for the portland cement are greater than those of any of the blends up to a paste age of 6 days. At a paste age of 6 days the heats of hydration of the 25 per cent blend and the portland cement are about the same.

Rate-of-heat-liberation test results

31. The rates of heat liberation for these blends are shown on fig. 7. The maximum rates for all the pastes occur between 8 and 13 hours. The rate curves of the blends do not occur within the portland-cement rate curve and the peaks, with reference to portland cement, move to the left as the blends become richer in natural cement until the blend containing 50 per cent natural cement is reached, where two peaks are found. The larger peak occurs between 8 and 9 hours and the smaller peak

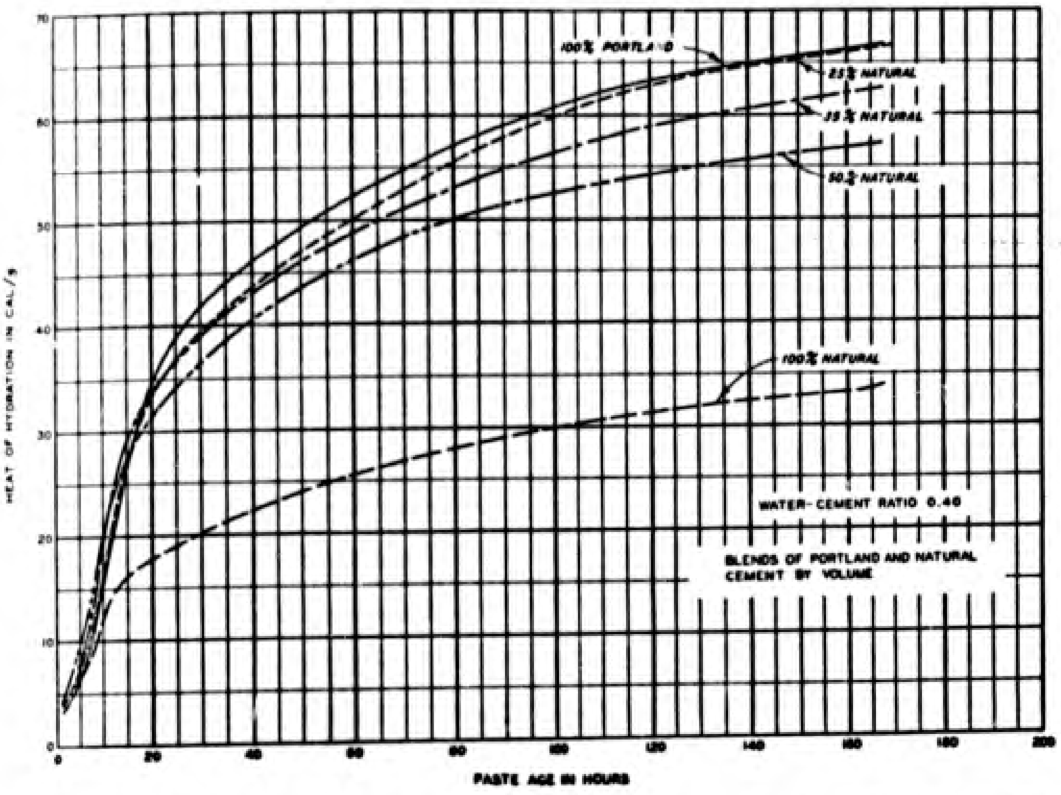



Fig. 6. Heat of hydration determined by conduction-calorimeter method

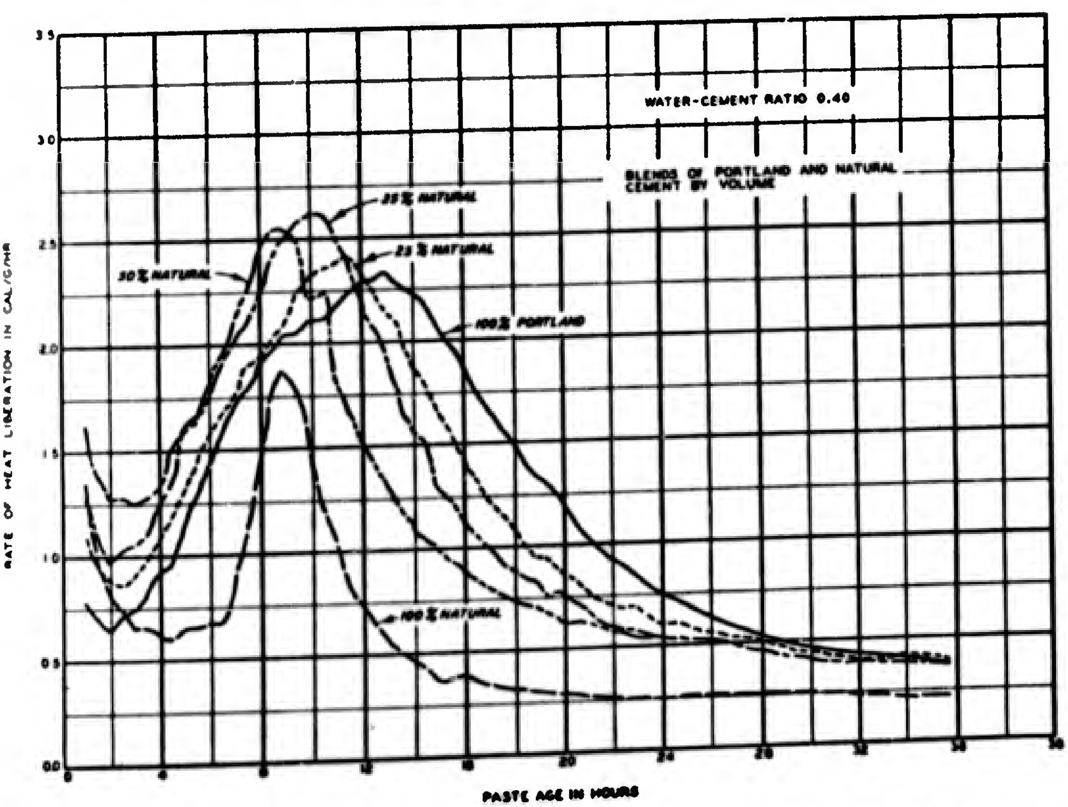



Fig. 7. Rate of heat liberation, conduction-calorimeter method

between 10 and 11 hours. The rate curves are, on the whole, smooth.

## Comparison of Results of the Three Methods

### General discussion

32. The heat of hydration results at paste ages of 3 and 7 days are presented in table 15, and on fig. 8. Heat-of-hydration values at

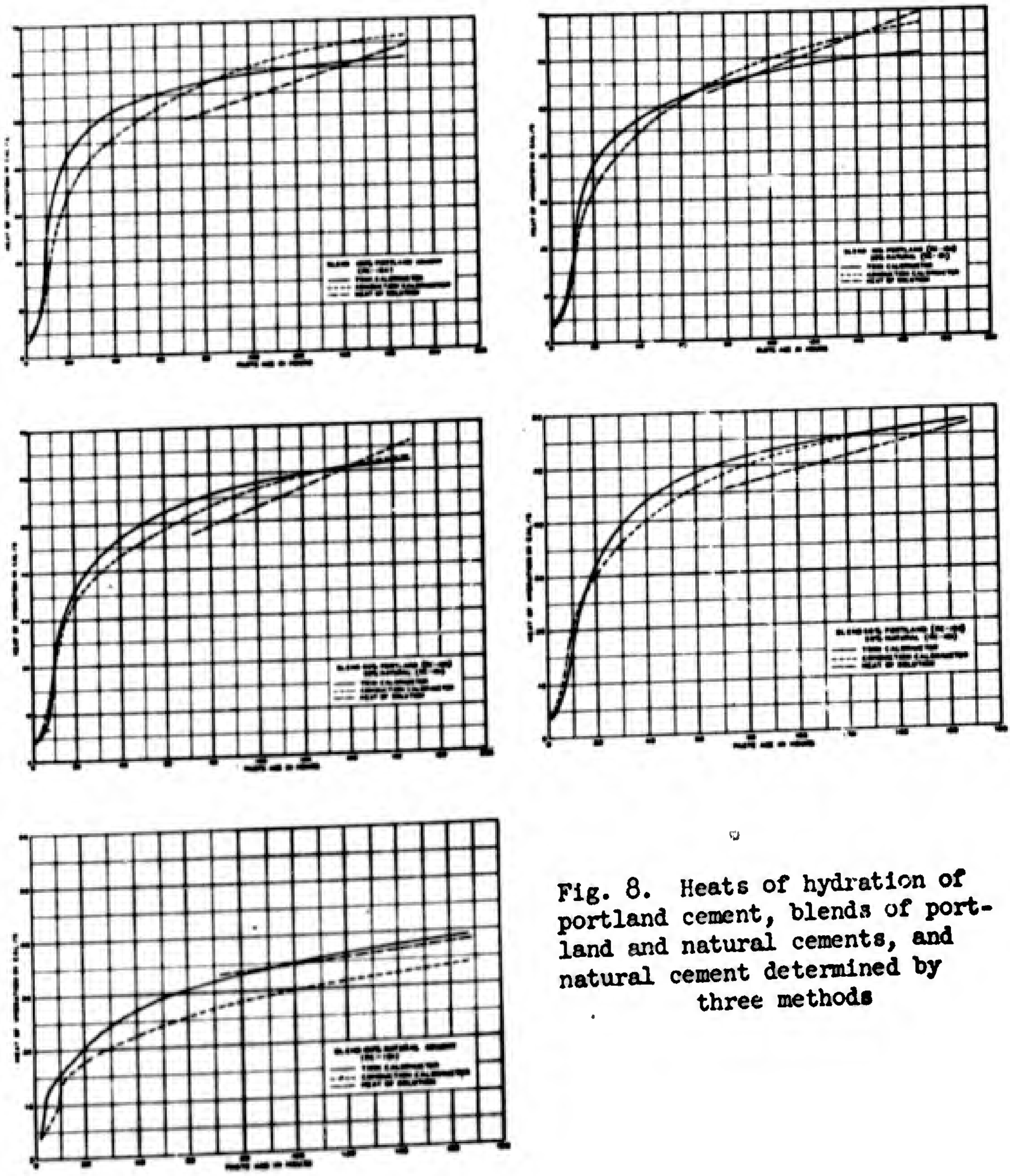


Fig. 8. Heats of hydration of portland cement, blends of portland and natural cements, and natural cement determined by three methods

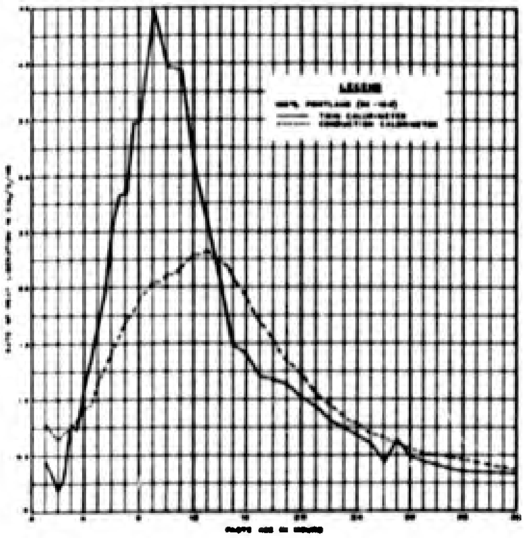
3 days age are uniformly higher when determined by the twin calorimeter than when determined by the conduction calorimeter. The heat-of-solution method gave the lowest value for four of the five materials; for 100 per cent natural cement it gave the highest value. Fig. 9 indicates the rate of heat liberation. The maximum rate of heat liberation was always greater for the twin-calorimeter method and occurred somewhat earlier than the maximum rate produced by the conduction-calorimeter method. At a paste age of 7 days a comparison of the results is not as consistent; however, the precision of the results appears to be adequate.

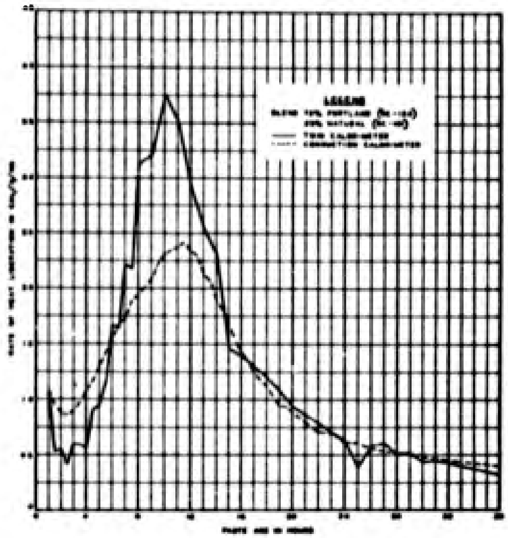
### Precision of the three methods of test

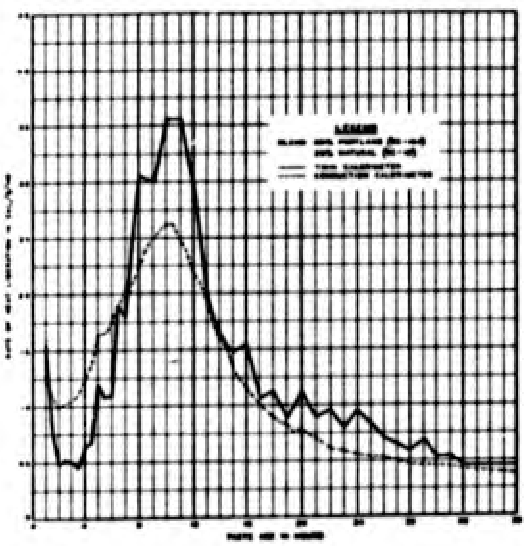
33. The study did not contemplate a statistical analysis of the three methods of test, but an estimate of the precision may be gained through consideration of the errors involved and examination of the data obtained. In examining the data it is of great importance to bear in mind the fact that the three different test methods were not run concurrently and that more than a year elapsed between the twin-calorimeter determinations and the conduction-calorimeter determinations.

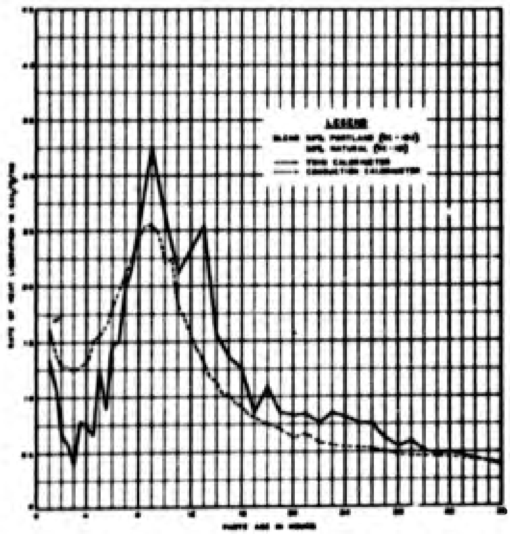
34. Heat-of-solution method. The errors involved in this procedure were discussed in paragraphs 6 and 8. However, the most important error encountered in the modification used in this work was in the assumption that the amount of material that will be dissolved by the acids is dependent only upon the time the material is in contact with the acid and not upon the paste age or any other factor. This assumption is not entirely valid. For the tests reported here, the average difference between duplicate determinations was approximately 4 cal per g; the maximum difference was 7 cal per g . The precision of this work may, therefore, be taken to be ± 2 cal per g . Additional studies involving different materials, using this modified method, have shown an average difference between duplicate determinations of approximately 10 cal per g or a precision of approximately ± 5 cal per g . The precision did not seem to vary with paste age.

35. Continuous heat evolution methods. The precision of these test methods is dependent upon the degree of freedom from two different









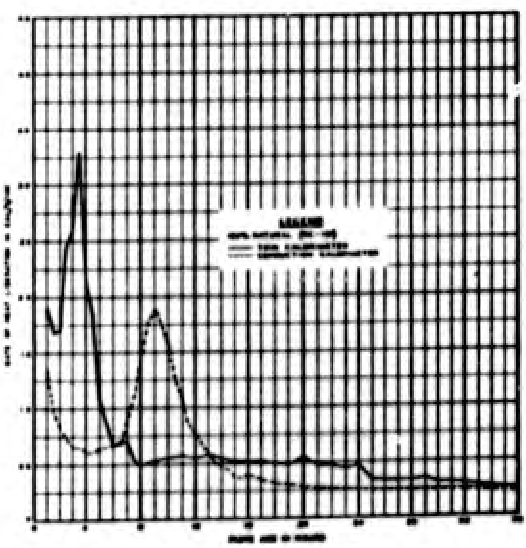


Fig. 9. Rates of heat liberation of portland cement, blends of portland and natural cements, and natural cement determined by two methods

types of errors. The first is the type normally encountered in the unmodified heat-of-solution method, in preparing and handling the paste. These errors are independent of the paste age and will have a magnitude of approximately ± 0.5 cal per g . The second type of error is caused by the measuring circuit and the fluctuations in the ambient conditions. These errors are cumulative and their effect upon the precision is dependent upon the duration of the test run.

36. Twin-calorimeter method. The measuring circuit for this method was manually controlled, and no control at all was exercised on the ambient conditions. The least reading of the temperature that can be considered as reliable is 0.25 C which corresponds to a heat release of 0.5 cal per g per day. This is about twice the hydration rate for an average cement at a paste age of 28 days. The error due to temperature measurement would therefore be at least 0.75 at 3 days and 1.75 at 7 days. Total expected precision would be ± 1.25 at 3 days and ± 2.25 at 7 days if the ambient conditions were controlled. For this work, it is estimated that the precision at a paste age of 7 days was about equal to or slightly better than that found for the modified heat-of-solution method.

37. Conduction-calorimeter method. The measurement circuit and ambient conditions were adequately and automatically controlled. The water bath temperature fluctuation was less than 0.01 C which corresponds to a recorder variation of 0.001 ohm-difference. The smallest reliable reading of the recorder was found to be 0.003 ohm-difference. Therefore the water bath temperature fluctuation is not a factor to be considered in estimating the precision and the possible duration of a test run. The value 0.003 ohm-difference corresponds to a heat release of approximately 0.20 cal per g per day, which is a little less than the expected heat release of an average cement at a paste age of 28 days. The total expected precision would be ± 0.8 cal per g at 3 days and ± 1.2 cal per g at 7 days. Other work, with other materials, performed with the conduction calorimeter, has indicated that these expected precisions are realistic, but low by approximately 0.5 cal per g . The expected precision at 28 days would be at least ± 3.3, but it is important to

remember that the percentage error for the heat released at that age would be about 50 per cent.

## PART IV: CONCLUSIONS

38. The following conclusions may be drawn from the results obtained in this work:

- a. The agreement between the results obtained using the three methods is adequate and within the limits of the expected precision of the test methods.
- b. In determination of the heat of hydration of slowly reacting materials, the conduction calorimeter is the more precise instrument at early ages. For tests at later ages the heat-of-solution method should be used. For portland cements, the conduction calorimeter may be regarded as a precision instrument up to a paste age of 7 days only, and its precision would be equal to that of the heat-of-solution method.
- c. The twin-calorimeter method, as used in this work, was inadequately controlled. It is believed that the necessary changes in equipment and method would be very expensive compared to the cost of development of the conduction calorimeter. The rate of heat liberation and the total heat of hydration for both methods proved to be similar.
- d. The rate of heat liberation may be used to distinguish between cements, and certainly to determine the effects of various materials blended with the cement.
- e. The determination of the heat of hydration by the conduction calorimeter is more involved than by the heat-of-solution method. The conduction-calorimeter determination requires the determination of the immediate heat of hydration and the determination of the specific heat of the sample. If the rate of heat liberation is not needed, the specific heat determination may be omitted.
- f. Further development of the conduction calorimeter to increase its precision and thereby increase the age at which reliable results may be obtained would involve a more sensitive detecting and recording system (the recorder should have several ranges), and a more precise control on the temperature of the water bath. Increasing the mass of the sample would also be helpful, particularly if the recorder had several ranges.
- g. It is suggested that for conduction-calorimeter determinations carried to paste ages in excess of 7 days, the sample be removed from the calorimeter at an age of 3 days and stored in a water bath held at the same temperature as the calorimeter water bath. The sample would be returned to the calorimeter at the desired paste age.

## REFERENCES


1. Carlson, Roy W., "The vane calorimeter," Proceedings, American Society for Testing Materials, vol 34, Part II, p 322 (1934).

2. Corps of Engineers, Waterways Experiment Station, "Tests of blends of portland and natural cements," unnumbered technical memorandum, Vicksburg, Mississippi, June 1944.

3. __________, "Effects of natural cement on shrinkage characteristics of mass concrete - Buggs Island Dam," unnumbered technical memorandum, Vicksburg, Mississippi, November 1948.

4. __________, "Handbook for concrete and cement," Vicksburg, Mississippi, August 1949.

5. __________, "Tests of commercially available cementitious materials," Technical Memorandum No. 6-335, Vicksburg, Mississippi, December 1951.

6. __________, "Tests of blends of portland cement with masonry cement," Technical Memorandum No. 6-359, Vicksburg, Mississippi, May 1953.

7. Lerch, William, "The influence of gypsum on the hydration and properties of portland cement pastes," Proceedings, American Society for Testing Materials, vol 46, p 1252 (1946); Research Laboratory, Portland Cement Association, Bulletin No. 12, 1946.

8. Newman, Edwin S., National Bureau of Standards, correspondence on file at Waterways Experiment Station.

Table 1

Results of Chemical Analyses of Cements

| Constituent | Portland Cement RC-184 % | Natural Cement RC-161 % |
| --- | --- | --- |
| $SiO_2$ | 22.8 | 20.8 |
| $Al_2O_3$ | 4.1 | 4.3 |
| $Fe_2O_3$ | 4.0 | 2.4 |
| CaO | 63.3 | 47.1 |
| MgO | 2.6 | 12.9 |
| $SO_3$ | 1.8 | 2.4 |
| Loss on ignition | 0.9 | 9.9 |
| $Na_2O$ | 0.09 | 0.21 |
| $K_2O$ | 0.60 | 1.0 |
| Insoluble residue | 0.48 | 86.1 |
| Total alkalies as $Na_2O$ | 0.48 | 0.87 |
| Calculated compounds | | |
| $C_3S$ | 46 | ----- |
| $C_2S$ | 31 | ----- |
| $C_3A$ | 4 | ----- |
| $C_4AF$ | 12 | ----- |
| $CaSO_4$ | 3 | ----- |

## Table 2

Typical Data Sheet for Heat-of-hydration Test by Heat-of-solution Method

mple: Natural Cement, Blend E (100% RC-161), 7 Days Age
te: 6/21/50 Initials: C.B.

| Weights | Trial I | | Trial II | |
|---|---|---|---|---|
| W, calorimeter sample | 4.1350 g | | 4.1330 g | |
| | Ignition | | Ignition | |
| | Before | After | Before | After |
| Crucible and sample | 28.9606 g | 27.5895 g | 28.7860 g | 27.4667 g |
| Crucible (I and II) | 24.8969 g | 24.8969 g | 24.7409 g | 24.7409 g |
| Sample (2 - 3) | 4.0637 g | 2.6926 g | 4.0451 g | 2.7258 g |
| Ignition ratio (after/before) | | 0.66260 g | | 0.67306 g |
| $W_1$, ign calorimeter sample (1 x 5) | | 2.7399 g | 2.7834 g | |

| Determination Trial I, Room Temp 22.70 C | | | | | Determination Trial II, Room Temp 23.30 C | | | |
|---|---|---|---|---|---|---|---|---|
| Time min | °B | Diff | °C | | Time min | °B | Diff | °C |
| 15 | 0.433 | ----- | 22.663 | | 15 | 1.106 | ----- | 23.336 |
| 20 | 0.475 | 0.042 | 22.705 | $\theta_o$ | 20 | 1.148 | 0.042 | 23.378 |
| 25 | 0.517 | 0.042 | 22.747 | $\theta_1$ | 25 | 1.190 | 0.042 | 23.420 |
| 26 | 2.080 | 1.563 | 24.310 | $\theta_1$ | 26 | 3.620 | 2.430 | 25.850 |
| 27 | 3.690 | 1.610 | 25.920 | $\theta_2$ | 27 | 4.460 | 0.840 | 26.690 |
| 28 | 3.790 | 0.100 | 26.020 | $\theta_3$ | 28 | 4.513 | 0.053 | 26.743 |
| 29 | 3.825 | 0.035 | 26.055 | $\theta_4$ | 29 | 4.540 | 0.027 | 26.770 |
| 30 | 3.841 | 0.016 | 26.071 | $\theta_5$ | 30 | 4.556 | 0.016 | 26.786 |
| 35 | 3.897 | 0.056 | 26.127 | $\theta_{10}$ | 35 | 4.610 | 0.054 | 26.840 |
| 40 | 3.932 | 0.035 | 26.162 | $\theta_{15}$ | 40 | 4.647 | 0.037 | 26.877 |
| 45 | 3.962 | 0.030 | 26.192 | $\theta_{20}$ | 45 | 4.680 | 0.033 | 26.910 |
| 50 | 3.989 | 0.027 | 26.219 | $\theta_{25}$ | 50 | 4.710 | 0.030 | 26.940 |
| 55 | 4.014 | 0.025 | 26.244 | $\theta_n$ | 55 | 4.740 | 0.030 | 26.970 |

### Formulae

°B = 22.230 °C

$$R = R_o - VrTx + K(\theta xTx - \theta rTx)$$

$$C = \frac{W(256.1 + 0.1\,(30 - t) + 0.12(T - t))}{R}$$

$$H_1 = (RC/W_1) - 0.2(T - t_d)$$

$$H_2 = (RC/W_1) - 0.4(T - t_h) - 0.3(t_d - t_h)$$

$$H_h = H_1 - H_2 + 0.1(25.0 - t_h)$$

Table 3

Typical Calculation Sheet for Heat-of-hydration Test by Heat-of-solution Method

Sample: Natural Cement, Blend E (100% RC-161), 7 Days Age
Date: 6/21/50 Initials: C.B.

| | Trial I | Trial II |
|---|---|---|
| $R_o$ | 3.497 | 3.550 |
| $V_aT_x$ | 0.246 | 0.252 |
| K (assumed) | 0.0045 | 0.0045 |
| $0.1\ \theta_i$ | 2.275 | 2.342 |
| $0.2\ \Sigma\theta_1 \ldots$ | 36.104 | 37.282 |
| $\Sigma\theta_{10}$ | 104.700 | 107.567 |
| $0.5\ \theta_n$ | 13.122 | 13.485 |
| $\theta_xT_x$ | 156.201 | 160.676 |
| $\theta_aT_x$ | 136.230 | 140.268 |
| Diff | 19.971 | 20.408 |
| K (Diff) | 0.090 | 0.092 |
| R | 3.335 | 3.390 |
| $W_i$ | 2.7399 | 2.7818 |
| C | 398.92 | 398.92 |
| $RC/W_i$ | 485.56 | 486.14 |
| T | 22.70 | 23.30 |
| $t_d$ | 26.70 | 26.70 |
| $t_h$ | 26.24 | 26.97 |
| $H_1$ | 525.60 | 525.60 |
| $0.4(T - t_h)$ | +1.42 | +1.47 |
| $0.3(t_d - t_h)$ | -0.14 | +0.08 |
| $H_2$ | 487.12 | 487.69 |
| $H_1 - H_2$ | 38.48 | 37.91 |
| $0.1(25.00 - t_h)$ | -0.12 | -0.20 |
| $H_h$ | 38.36 | 37.71 |
| Average | 38.04 | |

Table 4

Typical Data Sheet for Specific Heat Test

ple: Natural and Portland Cements, Blend D (50:50 RC-161 and RC-184) Age 1 hour
e: 1/2/51

Initials: H.H., C.D.

| Weights | Trial I | Trial II |
|---|---|---|
| Weight of kerosene, $W_k$ | 312.5 g | 312.5 g |
| Sample weight, $W_p$ | 32.93 g | 32.99 g |

Determination Trial I
Room Temp 26.40 C

| | Time min | °B | Diff | °C |
|---|---|---|---|---|
| | 20 | 0.355 | ----- | 5.665 |
| | 21 | 0.408 | 0.053 | 5.718 |
| | 22 | 0.460 | 0.052 | 5.770 |
| | 23 | 0.511 | 0.051 | 5.821 |
| .2 | 23.2 | 0.522 | 0.011 | 5.832 |
| .4 | 23.4 | 0.608 | 0.086 | 5.918 |
| .6 | 23.6 | 0.778 | 0.170 | 6.088 |
| .8 | 23.8 | 1.050 | 0.272 | 6.360 |
| | 24 | 1.310 | 0.260 | 6.620 |
| | 25 | 2.070 | 0.760 | 7.380 |
| | 26 | 2.210 | 0.140 | 7.520 |
| | 27 | 2.276 | 0.066 | 7.586 |
| | 28 | 2.326 | 0.050 | 7.636 |
| | 29 | 2.371 | 0.045 | 7.681 |
| | 30 | 2.414 | 0.043 | 7.724 |
| | 31 | 2.455 | 0.041 | 7.765 |
| | 32 | 2.495 | 0.040 | 7.805 |
| | 33 | 2.535 | 0.040 | 7.845 |

Determination Trial II
Room Temp 27.30 C

| | Time min | °B | Diff | °C |
|---|---|---|---|---|
| | 20 | 1.256 | ----- | 6.566 |
| $\theta_o$ | 21 | 1.307 | 0.051 | 6.617 |
| | 22 | 1.358 | 0.051 | 6.668 |
| $\theta_1$ | 23 | 1.409 | 0.051 | 6.719 |
| $\theta_{0.2}$ | 23.2 | 1.419 | 0.010 | 6.729 |
| $\theta_{0.4}$ | 23.4 | 1.450 | 0.031 | 6.760 |
| $\theta_{0.6}$ | 23.6 | 1.742 | 0.292 | 7.052 |
| $\theta_{0.8}$ | 23.8 | 2.012 | 0.270 | 7.322 |
| $\theta_1$ | 24 | 2.334 | 0.322 | 7.644 |
| $\theta_2$ | 25 | 2.989 | 0.655 | 8.299 |
| $\theta_3$ | 26 | 3.121 | 0.132 | 8.431 |
| $\theta_4$ | 27 | 3.192 | 0.071 | 8.502 |
| $\theta_5$ | 28 | 3.242 | 0.050 | 8.552 |
| $\theta_n$ | 29 | 3.288 | 0.046 | 8.598 |
| | 30 | 3.330 | 0.042 | 8.640 |
| $\theta_r$ | 31 | 3.372 | 0.042 | 8.682 |
| | 32 | 3.413 | 0.041 | 8.723 |

Formulae

°B = 5.310 °C

$$R = R_o - VrTx + K(\theta xTx - \theta rTx)$$

$$C = \frac{W(256.1 + 0.1(30 - t) + 0.12(T - t))}{R}$$

$$H_1 = (RC/W_1) - 0.2(T - t_d)$$

$$H_2 = (RC/W_1) - 0.4(T - t_h) - 0.3(t_d - t_h)$$

$$H_h = H_1 - H_2 + 0.1(25.0 - t_h)$$

## Table 5

**Typical Calculation Sheet for Specific Heat Test**

Sample: Natural and Portland Cements, Blend D (50:50 RC-161 and RC-184)
Age: 1 hour

Date: 1/2/51 Initials: H.H., C.D.

| | Trial I | Trial II | Trial III |
|---|---|---|---|
| $R_o$ | 1.903 | 1.879 | 1.713 |
| $V_rT_x$ | 0.280 | 0.252 | 0.240 |
| $V_a - V_r$ | 0.012 | 0.009 | 0.010 |
| $\theta_r - \theta_a$ | 2.035 | 2.014 | 1.843 |
| K | 0.0059 | 0.0045 | 0.0054 |
| $0.1\ \theta_1$ | 0.582 | 0.672 | 0.696 |
| $0.2\ \Sigma\theta_{0.2}\cdots$ | 8.812 | 10.159 | 10.950 |
| $\Sigma\theta_1$ | 37.803 | 33.784 | 34.188 |
| $0.5\ \theta_n$ | 3.862 | 4.299 | 4.335 |
| $\theta_xT_x$ | 51.059 | 48.914 | 50.169 |
| $\theta_rT_x$ | 54.635 | 52.092 | 52.506 |
| Diff | -3.576 | -3.178 | -2.337 |
| K(Diff) | -0.021 | -0.014 | -0.013 |
| R | 1.602 | 1.613 | 1.460 |
| $W_k$ | 312.5 | 312.5 | 311.7 |
| $W_p$ | 32.93 | 32.99 | 31.07 |
| $T_1$ | 5.821 | 6.719 | 6.957 |
| $T_e$ | 7.423 | 8.332 | 8.417 |
| $T_p$ | 26.40 | 27.30 | 26.75 |
| $\Delta T$ | 18.98 | 18.97 | 18.33 |
| $\Delta T/R$ | 11.848 | 11.761 | 12.555 |
| $(\Delta T/R)\ W_p$ | 390.2 | 388.0 | 390.1 |
| $W_kC_k$ | 146.9 | 146.9 | 146.5 |
| $W_kC_k + E$ | 149.6 | 149.6 | 149.2 |
| $C_p$ | 0.3834 | 0.3856 | 0.3825 |
| Avg $C_p$ | | 0.384 ± 0.001 | |

$C_k = 0.470$ $E = 2.70$

Formulae: $(W_kC_k + E)R = W_pC_p(\Delta T)$; $\Delta T = T_p - T_e = T_p - (T_1 + R)$

Table 6

Typical Data and Calculations for Determination of Immediate Heat of Hydration

Material: Natural and portland cements, blend B (25% RC-161, 75% RC-184)
Formula: $(W_w + E)\Delta T_w = W_c C_c \Delta T_c + H_t$
Calorimeter water equivalent (E) = 17.09
Specific heat of material ($C_c$) = 0.186 cal/g/C

Date: 10-7-50

| Time Interval min | Temp C | Temp Change $\Delta T_w$ C | $(W_w + E)$ $\Delta T_w$ cal | Temp Change $\Delta T_c$ C | $W_c C_c \Delta T_c$ cal | Total Heat Liberated $H_t$ cal | Heat Liberated in Period $H_i$ cal/period | Heat of Hydration $H_h$ cal/g | Rate of Heat Liberated $H_r$ cal/g/hr |
|---|---|---|---|---|---|---|---|---|---|
| **Run 1** | | | | | | | | | |
| Weight of water ($W_w$): 120.01 g; Temperature of water ($T_w$): 19.38 C; $W_w + E$ = 137.10 | | | | | | Weight of material ($W_c$): 299.99 g; Temperature of material ($T_c$): 26.38 C; $W_c C_c$ = 55.80 | | | |
| 5 | 23.08 | 3.70 | 507 | 3.30 | 184 | 323 | 323 | 1.077 | 12.92 |
| 10 | 24.61 | 5.23 | 717 | 1.77 | 99 | 618 | 295 | 0.983 | 11.80 |
| 15 | 25.21 | 5.83 | 799 | 1.17 | 65 | 734 | 116 | 0.387 | 4.64 |
| 20 | 25.58 | 6.20 | 850 | 0.80 | 45 | 805 | 71 | 0.237 | 2.84 |
| 25 | 25.82 | 6.44 | 883 | 0.56 | 31 | 852 | 47 | 0.157 | 1.88 |
| 30 | 26.01 | 6.63 | 909 | 0.37 | 21 | 888 | 36 | 0.120 | 1.44 |
| | | | | | | | Total | 2.961 | |
| **Run 2** | | | | | | | | | |
| Weight of water ($W_w$): 120.01 g; Temperature of water ($T_w$): 18.39 C; $W_w + E$ = 137.10 | | | | | | Weight of material ($W_c$) = 300.00 g; Temperature of material ($T_c$): 26.34 C; $W_c C_c$ = 55.80 | | | |
| 5 | 22.32 | 3.93 | 539 | 4.02 | 224 | 315 | 315 | 1.050 | 12.60 |
| 10 | 24.03 | 5.64 | 773 | 2.31 | 129 | 644 | 329 | 1.097 | 13.16 |
| 15 | 24.61 | 6.22 | 853 | 1.73 | 97 | 756 | 112 | 0.373 | 4.48 |
| 20 | 24.93 | 6.54 | 897 | 1.41 | 79 | 818 | 62 | 0.207 | 2.48 |
| 25 | 25.17 | 6.78 | 930 | 1.17 | 65 | 865 | 47 | 0.157 | 1.88 |
| 30 | 25.35 | 6.96 | 954 | 0.99 | 55 | 899 | 34 | 0.113 | 1.36 |
| | | | | | | | Total | 2.997 | |
| **Run 3** | | | | | | | | | |
| Weight of water ($W_w$): 120.00 g; Temperature of water ($T_w$): 18.59 C; $W_w + E$ = 137.09 | | | | | | Weight of material ($W_c$): 299.99 g; Temperature of material ($T_c$): 27.06 C; $W_c C_c$ = 55.80 | | | |
| 5 | 22.62 | 4.03 | 552 | 4.44 | 248 | 304 | 304 | 1.013 | 12.16 |
| 10 | 24.54 | 5.95 | 816 | 2.52 | 141 | 675 | 371 | 1.237 | 14.84 |
| 15 | 25.09 | 6.50 | 891 | 1.97 | 110 | 781 | 106 | 0.353 | 4.24 |
| 20 | 25.39 | 6.80 | 932 | 1.67 | 93 | 839 | 58 | 0.193 | 2.32 |
| 25 | 25.61 | 7.02 | 962 | 1.45 | 81 | 881 | 42 | 0.140 | 1.68 |
| 30 | 25.79 | 7.20 | 987 | 1.27 | 71 | 916 | 35 | 0.117 | 1.40 |
| | | | | | | | Total | 3.053 | |

Table 7

Heat of Hydration Determined by Twin-calorimeter Method

Natural and portland cements, blend D (50:50 RC-161 and RC-184)

Weight of paste = 297.9 g | Weight of water = 108.4 g | Ignition ratio = 0.6997

| (1) Elapsed Time hr | (2) Watt-hour Meter Reading whr | (3) Watt-hour Meter Diff | (4) Power Input (3)xVolt Factor | (5) Subtotal | (6) Voltage | (7) Temperatures Cement F | (8) Temperatures Cement C | (9) Temperatures Water F | (10) Temperatures Water C | (11) Amb F | (12) Heat Input cal/period (4)x860 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 133730.4 | 8.4 | 0.151 | 1.566 | 116.0 | 86.8 | 30.44 | 86.8 | 30.44 | 77.4 | 129.9 |
| 5.5 | 36.0 | 5.6 | 0.101 | 1.667 | 115.5 | 87.8 | 31.00 | 87.8 | 31.00 | 77.7 | 86.9 |
| 6.0 | 45.8 | 9.8 | 0.176 | 1.843 | 116.0 | 89.0 | 31.67 | 89.0 | 31.67 | 77.8 | 151.4 |
| 6.5 | 55.8 | 10.0 | 0.180 | 2.023 | 116.0 | 90.2 | 32.33 | 90.2 | 32.33 | 78.0 | 154.8 |
| 7.0 | 69.2 | 13.4 | 0.241 | 2.264 | 116.0 | 91.8 | 33.22 | 91.8 | 33.22 | 78.1 | 207.3 |
| 7.5 | 84.0 | 14.8 | 0.263 | 2.527 | 117.0 | 93.8 | 34.33 | 93.8 | 34.33 | 78.4 | 226.2 |
| 8.0 | 801.8 | 17.8 | 0.320 | 2.847 | 116.0 | 96.0 | 35.56 | 96.2 | 35.67 | 78.4 | 275.2 |

| (13) Specific Heat of Water cal/g/C | (14) Specific Heat of Water cal/C | (15) Temp Input C (12)/(14) | (16) Temp Rise Water, C $(10)_2-(10)_1$ | (17) Temp Loss Water, C (15)-(16) | (18) Recorded Rise Cement, C $(8)_2-(8)_1$ | (19) Corrected Increase Cement, C (17)+(18) | (20) Specific Heat of Paste cal/g/C (Ign Wt) | (21) Heat of Hydration cal/g/period (20)x(19) | (22) Rate of Hydration cal/g/hr (21)/Period | (23) Total Heat cal/g |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.998 | 108.2 | 1.20 | 0.38 | 0.82 | 0.38 | 1.20 | 0.527 | 0.63 | 1.26 | 6.75 |
| 0.998 | 108.2 | 0.80 | 0.56 | 0.24 | 0.56 | 0.80 | 0.526 | 0.42 | .84 | 7.17 |
| 0.998 | 108.2 | 1.40 | 0.67 | 0.73 | 0.67 | 1.40 | 0.525 | 0.74 | 1.48 | 7.91 |
| 0.998 | 108.2 | 1.43 | 0.66 | 0.77 | 0.66 | 1.43 | 0.523 | 0.75 | 1.50 | 8.66 |
| 0.998 | 108.2 | 1.92 | 0.89 | 1.03 | 0.89 | 1.92 | 0.522 | 1.00 | 2.00 | 9.66 |
| 0.998 | 108.2 | 2.09 | 1.11 | 0.98 | 1.11 | 2.09 | 0.522 | 1.09 | 2.18 | 10.75 |
| 0.998 | 108.2 | 2.54 | 1.34 | 1.21 | 1.23 | 2.44 | 0.520 | 1.27 | 2.54 | 12.02 |

## Table 8

Heat of Hydration Determined by Conduction-calorimeter Method

Portland cement, blend A (100% RC-184)

Calorimeter constants: 1 ohm - 0.218 cal/sec (A) and = 9.36 C (B);
zero reading = 0.192 ohm or 0.042 cal/sec (C)

Weight of paste = 289.5 g — Ignition ratio = 0.7227
Ignited weight of paste = 209.2 g(D)

| (1) Elapsed Time hr | (2) Period Length hr | (3) Recorder Reading ohm | (4) Apparent Heat Conduction cal/sec (3)x(A) | (5) Actual Heat Conduction cal/sec (4)-(C) | (6) Heat Conduction cal/g (5)x(2)x3600/(D) | (7) Paste Temp C (3)x(B) |
|---|---|---|---|---|---|---|
| 22.5 | 0.5 | 0.461 | | | | 4.31 |
| | | 0.454 | 0.099 | 0.057 | 0.49 | |
| 23.0 | 0.5 | 0.447 | | | | 4.18 |
| | | 0.441 | 0.096 | 0.054 | 0.46 | |
| 23.5 | 0.5 | 0.434 | | | | 4.06 |
| | | 0.429 | 0.094 | 0.052 | 0.45 | |
| 24.0 | 0.5 | 0.421 | | | | 3.94 |
| | | 0.414 | 0.090 | 0.048 | 0.41 | |
| 24.5 | 0.5 | 0.411 | | | | 3.85 |
| | | 0.405 | 0.088 | 0.046 | 0.40 | |
| 25.0 | 0.5 | 0.400 | | | | 3.74 |

| (1) Elapsed Time hr | (8) Paste Temp Change C $(7)_1-(7)_2$ | (9) Specific Heat Paste cal/g/C | (10) Heat Stored in Paste cal/g (9)x(8) | (11) Heat Liberated cal/g (6)+(10) | (12) Heat of Hydration cal/g (11) | (13) Rate of Heat Liberation cal/g/hr (11)/(2) |
|---|---|---|---|---|---|---|
| 22.5 | | | | | 37.09 | |
| 23.0 | -0.13 | 0.47 | -.06 | 0.43 | 37.52 | 0.86 |
| 23.5 | -0.12 | 0.47 | -.06 | 0.40 | 37.92 | 0.80 |
| 24.0 | -0.12 | 0.47 | -.06 | 0.39 | 38.31 | 0.78 |
| 24.5 | -0.09 | 0.47 | -.04 | 0.37 | 38.68 | 0.74 |
| 25.0 | -0.11 | 0.47 | -.05 | 0.35 | 39.03 | 0.70 |

Table 9

Heat-of-solution Method

Temperature = 73 F

W/C = 0.40

| Blends of Cement (RC-184 Portland, RC-161 Natural) by Volume | Heat of Hydration, cal/g, at Age of | | | |
|---|---|---|---|---|
| | 3 Days | 7 Days | 14 Days | 28 Days |
| A (100% RC-184 0% RC-161) | 49.9 | 65.0 | 70.0 | 76.1 |
| B ( 75% RC-184 25% RC-161) | 52.9 | 69.4 | 71.5 | 74.1 |
| C ( 65% RC-184 35% RC-161) | 47.6 | 66.1 | 66.5 | 70.9 |
| D ( 50% RC-184 50% RC-161) | 45.7 | 56.4 | 63.4 | 66.1 |
| E ( 0% RC-184 100% RC-161) | 32.9 | 38.1 | 45.5 | 54.3 |

Table 10

Water-cement Ratio of the Pastes Tested by the Heat-of-solution Method

| Blends* of Cement (RC-184 Portland RC-161 Natural) by Volume | Water-cement Ratio at Age of | | | |
|---|---|---|---|---|
| | 3 Days | 7 Days | 14 Days | 28 Days |
| A (100% RC-184 0% RC-161) | 0.36 | 0.37 | 0.36 | 0.37 |
| B (75% RC-184 25% RC-161) | 0.37 | 0.39 | 0.37 | 0.38 |
| C (65% RC-184 35% RC-161) | 0.38 | 0.39 | 0.37 | 0.37 |
| D (50% RC-184 50% RC-161) | 0.39 | 0.40 | 0.37 | 0.38 |
| E (0% RC-184 100% RC-161) | 0.38 | 0.40 | 0.38 | 0.40 |

* Material was mixed for a W/C of 0.40, but as a result of grinding the paste, the W/C was reduced. The data shown above were calculated from the ignition ratios.

Table 11

Mean Specific Heats of Pastes, Calories Per Gram of Paste Per Degree Centigrade, of Blends of Portland and Natural Cements at Room Temperature and at Various Ages

W/C = 0.40

| Blend (% by Vol) | Paste Age | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 (Dry Cement Only) | | | 1 Hour | | | 1 Day | | | 3 Days | | | 7 Days | | |
| | C* | SD† | Calc‡ | C | SD | Calc | C | SD | Calc | C | SD | Calc | C | SD | Calc |
| A 100% Portland | .170 | .002 | ----- | .354 | .001 | ---- | .334 | .003 | ---- | .316 | .005 | ---- | .308 | .004 | ---- |
| B 25% Natural | .175 | .003 | .176 | .368 | .004 | .363 | .334 | .003 | .339 | .322 | .007 | .324 | .317 | .003 | .316 |
| C 35% Natural | .176 | .002 | .179 | .370 | .004 | .367 | .342 | .006 | .341 | .328 | .003 | .328 | .310 | .003 | .320 |
| D 50% Natural | .181 | .001 | .182 | .384 | .001 | .373 | .343 | .005 | .345 | .336 | .008 | .333 | .322 | .003 | .325 |
| E 100% Natural | .196 | .005 | ----- | .393 | .007 | ---- | .356 | .002 | ---- | .353 | .003 | ---- | .344 | .003 | ---- |

* C, specific heat.

† SD, standard deviation; each experimental determination of C was calculated on the basis of 3 to 5 runs.

‡ Calc, calculated value; these values for blends B, C, and D were based on the assumption of linearity.

Immediate Heat of Hydration ($H_h$)* and Rate of Heat Liberation ($H_r$)† of Blends of Portland and Natural Cements at Room Temperature and Water-cement Ratio of 0.40

| Blends of Cement (RC-184 Portland RC-161 Natural) by Volume | Heat of Hydration or Heat Liberation | Time Interval, min | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 15 | 20 | 25 | 30 | Total |
| A (100% RC-184 0% RC-161) | $H_h$ | 1.268 | 0.777 | 0.346 | 0.212 | 0.132 | 0.100 | 2.835 |
| | $H_r$ | 15.22 | 9.32 | 4.14 | 2.54 | 1.59 | 1.20 | |
| B (75% RC-184 25% RC-161) | $H_h$ | 1.047 | 1.106 | 0.371 | 0.212 | 0.150 | 0.118 | 3.004 |
| | $H_r$ | 12.56 | 13.28 | 4.45 | 2.52 | 1.80 | 1.41 | |
| C (65% RC-184 35% RC-161) | $H_h$ | 0.945 | 1.066 | 0.378 | 0.230 | 0.156 | 0.141 | 2.916 |
| | $H_r$ | 11.30 | 12.79 | 4.53 | 2.76 | 1.88 | 1.69 | |
| D (50% RC-184 50% RC-161) | $H_h$ | 1.004 | 0.932 | 0.476 | 0.245 | 0.185 | 0.159 | 3.001 |
| | $H_r$ | 12.05 | 11.19 | 5.71 | 2.95 | 2.22 | 1.90 | |
| E (0% RC-184 100% RC-161) | $H_h$ | 0.801 | 0.437 | 0.550 | 0.457 | 0.335 | 0.262 | 2.842 |
| | $H_r$ | 9.61 | 5.24 | 6.60 | 5.48 | 4.02 | 3.14 | |

* Calories per gram of cement.
† Calories per gram of cement per hour.

Table 13

Heat of Hydration ($H_h$)* and Rate of Heat Liberation ($H_r$)†

Twin-calorimeter Method

Temperature = 73 F, W/C = 0.40

| Paste Age Days | Blends of Portland (RC-184) and Natural (RC-161) Cements (Designated as % Portland Cement) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 100% | | 75% | | 65% | | 50% | | 0% | |
| | $H_r$ | $H_h$ | $H_r$ | $H_h$ | $H_r$ | $H_h$ | $H_r$ | $H_h$ | $H_r$ | $H_h$ |
| 1/2 | 3.07 | 30.30 | 2.91 | 25.47 | 2.98 | 25.12 | 2.33 | 22.35 | 0.54 | 16.37 |
| 1 | 0.78 | 45.67 | 0.64 | 40.79 | 0.96 | 39.67 | 0.82 | 35.99 | 0.48 | 22.43 |
| 2 | 0.18 | 53.51 | 0.27 | 49.50 | 0.23 | 49.87 | 0.26 | 45.78 | 0.24 | 28.68 |
| 3 | 0.08 | 56.69 | 0.13 | 53.8 | 0.16 | 54.53 | 0.10 | 50.40 | 0.11 | 31.87 |
| 4 | 0.07 | 58.56 | 0.11 | 56.69 | 0.09 | 57.22 | 0.09 | 52.82 | 0.10 | 34.31 |
| 5 | 0.06 | 60.01 | 0.04 | 58.46 | 0.10 | 59.53 | 0.08 | 54.60 | 0.07 | 35.96 |
| 6 | 0.06 | 61.48 | 0.03 | 59.47 | 0.07 | 61.11 | 0.05 | 55.95 | 0.05 | 37.45 |
| 7 | 0.04 | 62.38 | 0.05 | 60.55 | 0.06 | 62.09 | 0.04 | 56.98 | 0.08 | 39.12 |

* Calories per gram (ignited weight).
† Calories per gram per hour (ignited weight).

Table 14

Heat of Hydration ($h_h$)* and Rate of Heat Liberation ($H_r$)†

Conduction-calorimeter Method

Temperature = 73 F, W/C = 0.40

| Paste Age Days | Blends of Portland (RC-184) and Natural (RC-161) Cements (Designated as % Portland Cement) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 100% | | 75% | | 65% | | 50% | | 0% | |
| | $H_r$ | $H_h$ | $H_r$ | $H_h$ | $H_r$ | $H_h$ | $H_r$ | $H_h$ | $H_r$ | $H_h$ |
| 1/2 | 2.30 | 19.93 | 2.34 | 21.83 | 2.18 | 24.05 | 1.54 | 23.92 | 0.78 | 14.59 |
| 1 | 0.78 | 38.31 | 0.62 | 36.52 | 0.56 | 36.39 | 0.55 | 33.66 | 0.26 | 18.83 |
| 2 | 0.34 | 48.58 | 0.34 | 46.55 | 0.32 | 45.63 | 0.32 | 43.09 | 0.18 | 23.85 |
| 3 | 0.26 | 55.11 | 0.27 | 53.60 | 0.23 | 51.56 | 0.20 | 48.46 | 0.13 | 27.20 |
| 4 | 0.21 | 60.07 | 0.23 | 59.05 | 0.18 | 55.86 | 0.14 | 51.98 | 0.09 | 29.46 |
| 5 | 0.17 | 63.37 | 0.16 | 62.82 | 0.13 | 58.87 | 0.09 | 54.19 | 0.08 | 31.27 |
| 6 | 0.09 | 65.43 | 0.11 | 65.34 | 0.09 | 61.02 | 0.07 | 55.94 | 0.06 | 32.63 |
| 7 | 0.07 | 67.08 | 0.07 | 67.02 | 0.07 | 62.74 | 0.05 | 57.26 | 0.06 | 33.99 |

* Calories per gram (ignited weight).
† Calories per gram per hour (ignited weight).

Table 15

Comparison of the Heat-of-hydration Results Obtained by the Heat-of-solution, Twin-calorimeter, and Conduction-calorimeter Methods

| Blends of Cement (RC-184 Portland RC-161 Natural) by Volume | Test Method | Heat of Hydration cal/g at Paste Age of 3 Days | 7 Days |
|---|---|---|---|
| A (100% RC-184 0% RC-161) | Solution | 49.9 | 65.0 |
| | Twin | 56.7 | 62.4 |
| | Conduction | 55.1 | 67.1 |
| B (75% RC-184 25% RC-161) | Solution | 52.9 | 69.4 |
| | Twin | 53.8 | 60.6 |
| | Conduction | 53.6 | 67.0 |
| C (65% RC-184 35% RC-161) | Solution | 47.6 | 66.1 |
| | Twin | 54.5 | 62.1 |
| | Conduction | 51.6 | 62.7 |
| D (50% RC-184 50% RC-161) | Solution | 45.7 | 56.4 |
| | Twin | 50.4 | 57.0 |
| | Conduction | 48.5 | 57.3 |
| E (0% RC-184 100% RC-161) | Solution | 32.9 | 38.1 |
| | Twin | 31.9 | 39.1 |
| | Conduction | 27.2 | 34.0 |